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Innovative and Reliable Assessment of Polluted Stormwater Runoff for Effective Stormwater Management

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Abstract: This article examines the pollution dynamics in urban wet-weather runoff, addressing the statistical characterization and systematic classification of water quality characteristics as key aspects of sustainable and effective urban stormwater quality control and treatment measures. A reliable first flush methodology is applied to discrete water quality data of different pollution parameters from an Italian database for the identification of the Bivio Vela catchment's representative evolution of mean concentrations and the assessment of the required runoff volume to reduce stormwater pollutant concentrations to background levels. A comparison is carried out between results from two catchments with different land use types (industrial versus residential) and the complexity of the sewerage system, highlighting challenges in tracking pollution trends and delineating peculiar dynamics of different quality parameters in a specific geographic context. Despite appreciably different pollutant dynamics, both catchments achieve background levels for all the examined parameters after 6 mm runoff. The outcome of the analysis has clear implications for the design approach of sustainable stormwater management practices.

Keywords: stormwater; pollution; EMC; first flush; experimental data; control practices

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1. Introduction

Runoff is widely considered as the major transport vector of pollution generated in urban areas, negatively affecting the receiving environment via non-point source pollution. Pollutant dynamics in urban wet-weather runoff are influenced by several factors, including anthropogenic activities, degree of land development, land cover and land use, as well as rainfall patterns and geographic location/climate [1,2].

Many studies on stormwater quality show that the initial part of the runoff resulting from a rainfall event is often more contaminated than the subsequent part, i.e., the first foul flush (FF) phenomenon, and a variety of FF identification methods have been proposed in the relevant scientific literature, examining either the time–evolution of the concentration of different pollutants or the cumulative pollutant mass over the cumulative wet-weather runoff volume, e.g., [3–10].

Despite several sometimes unclear and subjective detection methods, academics, political decision makers and watershed managers unanimously acknowledge the potential usefulness of the FF concept for sustainable, efficient and cost-effective implementation of both conventional structural stormwater control practices and green infrastructure technologies, e.g., [11–17].

In order to realize this potential, the FF concept should lead to a suitable assessment of a highly contaminated stormwater volume, which is dangerous for the receiving environment and therefore requires treatment, using a quantitative and objective procedure.

Unfortunately, most of the procedures mentioned above involve a subjective/arbitrary estimation of the FF volume, and the lack of standardization and consistency in the analysis of stormwater quality time–evolution means that these methodologies cannot be adopted as an appropriate basis for the design and sizing criteria for stormwater quality control measures [18–20].

A unified FF objective definition and assessment method as well as systematic classification and identification of pollution characteristics are the basis for effective stormwater quality control and treatment measures [21].

Kang et al. [22,23] identify short-term and long-term pollution sources in an urban area. Short-term sources are related to the build-up of pollution occurring in dry weather conditions. These sources can be reduced by a subsequent rainfall event with adequate intensity and duration. The base or background level of pollution characterizing an urban area acts as a long-term source that cannot be reduced.

Bach et al. [24] introduce a reliable and objective method for the FF assessment, which also makes a distinction between short-term and long-term sources of urban wet-weather runoff pollution. By using this method, it is possible to assess the severely contaminated stormwater runoff volume, which is harmful to the environment, by analyzing the trend of the average concentrations of representative pollution parameters for subsequent parts of the runoff volume. For this purpose, an adequate number of real-event hydrographs and pollutographs is necessary. Non-parametric statistics are then adopted to determine a catchment's peculiar initial and background pollutant concentrations, the FF volume and its strength.

The analysis used for the statistical characterization of the mean concentration trend for subsequent increments of runoff allows the detection of representative pollutographs for an urban catchment. Synthetic pollutographs can be useful for a quick assessment of the potential environmental impact of the urban drainage system on the receiving natural body. Thus, they can be essential for studies that address environmental sustainability and protection of natural resources.

Todeschini et al. [25] applied the approach of Bach et al. [24] on discrete water quality data of different pollutant types acquired during a 3-year experimental campaign in an urban catchment of Pavia, Lombardy region, northern Italy. The investigation highlighted the fruitfulness and profitability of the statistical characterization and classification of water quality characteristics to guide decisions and sizing criteria for stormwater quality control measures. In this study, it is established that strict selection criteria for the adopted events and a well-conceived monitoring protocol are crucial for the reliability and robustness of the obtained results.

Water level and/or flow rate are commonly acquired with high frequency and adequate accuracy during monitoring campaigns in relation to sewerage. Conversely, despite considerable monitoring efforts, achieved water quality data are often limited or unreliable due to a lack of sample integrity, uncertainties and errors in the analytical process, with significant costs related to the monitoring equipment [26–29].

For an effective stormwater quality characterization, a proper monitoring program and sampling acquisition protocol are crucial. Monitoring campaigns should be performed over a long period of time, ideally not less than one year. Otherwise, the acquired data may fail to capture the impact of factors and processes that influence the release, destination and transport of pollutants on other time scales, such as seasonal behaviors. Various pollutants should be analyzed as detailed knowledge of the dynamics of different types of pollution, including organic and inorganic pollutants, heavy metals and nutrients, is essential in order to achieve effective improvement in the design and management of stormwater control and treatment practices [30,31]. And the main challenge remains to expand the knowledge acquired by taking into account conditions that continually modify over time due to increasing soil imperviousness, climate change, new materials and pollutants of emerging concern.

With the aim of further deepening knowledge of the pollutant dynamics in urban wet-weather runoff and exploring the definition of representative pollutographs, the current study addresses both the statistical characterization of the mean pollutant concentrations in slices of wet-weather runoff and the assessment of the FF volume considering experimental data acquired during long-term monitoring campaigns in an industrial catchment located in Pavia [32], which is close to the urban catchment examined in [25].

The availability of sound stormwater quality characterization in neighboring catchments with the same climatic features is a new and relevant outcome of this study that allows one to evaluate how different land use types of the territory (i.e., production versus residential use) and increasing complexity of the sewerage system affect representative pollutographs and FF volume and, therefore, influence the design approach of sustainable stormwater control practices and treatment systems.

2. Materials and Methods

2.1. Case Study and Data Acquisition

The case study catchment is an exclusively industrial district called Bivio Vela, with a total surface area of 85.93 ha. It is located on the eastern outskirts of Pavia, a town in the Lombardy region of northern Italy. The catchment hosts various production activities; it includes an artisan area, a major food plant producing rice, an area equipped for the distribution of goods and areas in which the production settlement plan (P.I.P.) of the municipality of Pavia provides for the establishment of further industrial activities. The catchment is divided into two sub-catchments, named SC1 and SC2 (Figure 1). The upstream SC1 has an area of 51.25 ha, while the downstream SC2 has an area equal to 34.68 ha. The current degree of imperviousness is equal 0.60 for SC1 and 0.36 for SC2, with a value of 0.50 for the entire catchment.

The area is served by a combined sewerage system, with a total length of pipes of about 6610 m. The slope of the sewer pipes ranges between 0.1% and 1.0%. The sewerage of SC1 is made of standard concrete pipes: circular pipes, with diameters between DN 300 and DN 600 mm, and ovoid pipes with diameters between DN 600/900 and DN 1400/2100 mm. The sewerage of SC2 consists of circular pipes: vitrified clay pipes for pipe diameters less than 600 mm and reinforced concrete pipes for pipe diameters between 700 and 1800 mm.

The sewerage system of SC1 delivers waste and stormwater to a pumping station, PS1. This station includes three motor pumps that in wet weather can drive a maximum flow rate equal to 130 L/s to the sewerage of SC2. This maximum flow corresponds to about 4 L/s per hectare of contributing impervious area as it complies with the current legislation of the Lombardy region (Regional Regulation of Lombardy Region n. 6/2019). In wet weather, the incoming flow rate from SC1 exceeding a value of 130 L/s is discharged through a combined sewer overflow (CSO1) into a receiving water course.

The sewer network of SC2 drains the area of the sub-catchment up to the final section of the system, where two pumping stations (PS2 and PS3) and a stormwater detention tank (SWDT) are installed. PS2 is equipped with two identical motor pumps working in parallel that provide an overall flow rate equal to 64 L/s. This station works in dry weather (when the incoming flow rate is less than 64 L/s). PS3 is downstream of PS2 and in direct communication with the SWDT. This station is activated in wet weather, when the incoming flow rate exceeds 64 L/s and stormwater overflows from the chamber of PS2 to the chamber of PS3; the activation of PS3 involves the deactivation of PS2. PS3 has two motor pumps working in parallel, identical to those of station PS2. PS3 operates in wet weather and it is used to empty the SWDT at the end of stormwater runoff. (The adoption of two different pumping stations in the final section of the system avoids the need to further lower the inlet flow rate in dry weather because the bottom of PS3, which also has the function to empty the SWDT, is two meters lower than that of PS2.) Overflow to the receiving water body occurs when the SWDT is full or when the incoming flow rate exceeds 360 L/s. The SWDT has a volume equal to 2375 m^3, corresponding to approximately 50 m^3 per hectare of contributing impervious area in accordance with the requirements of Regional Regulation of Lombardy Region n. 6/2019.

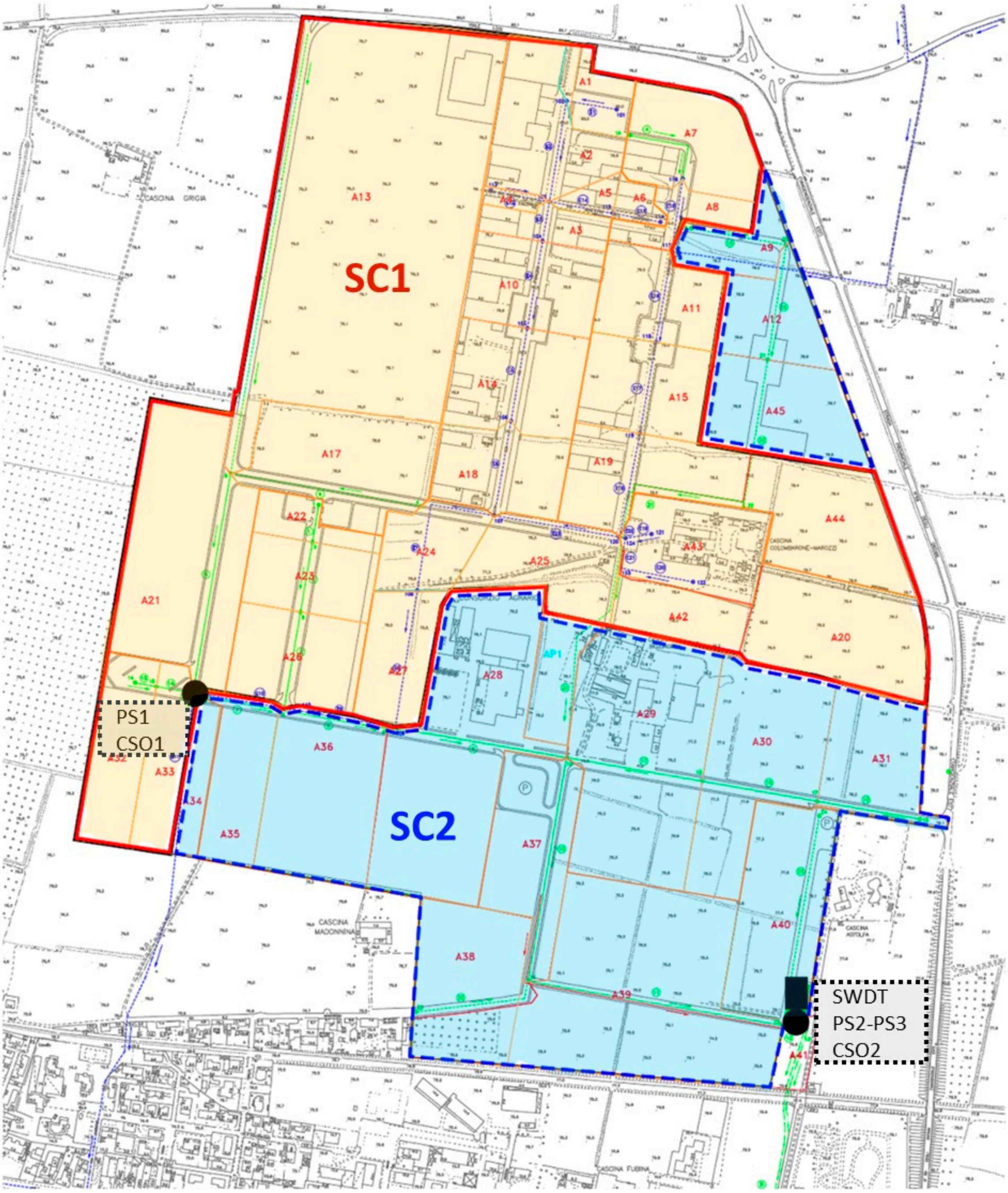

Figure 1. Map of Bivio Vela experimental catchment and sewerage system; SC1 (yellow color) is bordered with a continuous line, SC2 (blue color) with a dashed line.

Since 2007, the Bivio Vela catchment has been fitted with instruments for the quantitative and qualitative monitoring of rainfall-runoff processes as well as for the performance assessment of existing stormwater control practices. The instrumental equipment includes an SIAP tipping bucket rain gauge (SIAP, 40050 Villanova, Bologna, Italy) with 0.2 mm accuracy, an ISCO 4230 bubbler flow meter (ISCO, AST Analytica Srl, 16145 Genova, Italy) and an ISCO 6700 SR refrigerated automatic grab sampler. The flow meter probe and the sampling strainer are positioned at the closure of the system, immediately upstream of the overflow structure to chamber PS3 (Figure 2). More detailed information on the characteristics of the catchment, monitoring equipment, and data collection and sampling protocol is available in [32].

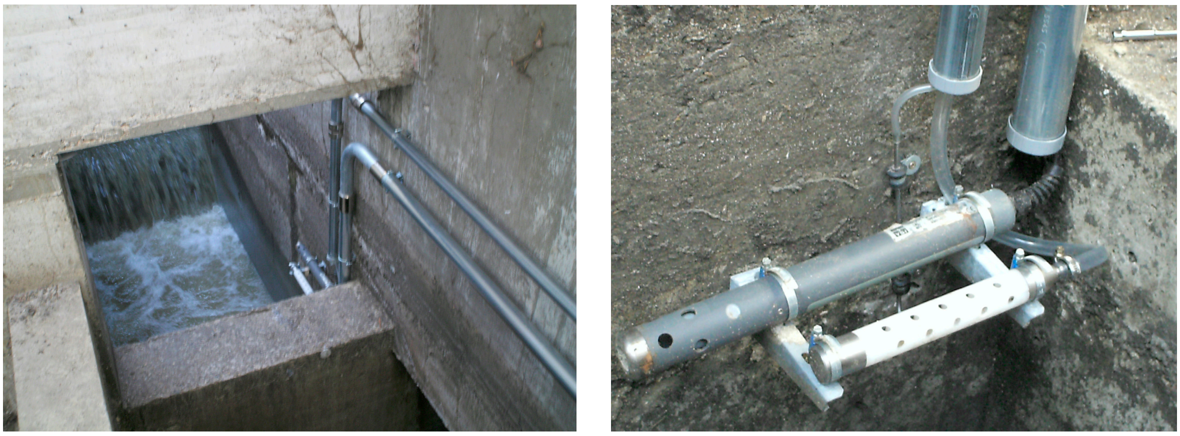

Figure 2. Positioning and detail of the monitoring equipment: bubble level meter and sampling probe.

Rainfall-runoff and water quality data were collected over a period of more than one year. The monitored events exhibit a wide range of relevant precipitation characteristics (i.e., total depth, total duration, maximum depth for different durations, mean intensity, duration of antecedent dry period).

The monitoring protocol involved different sample acquisition time distances: every 5 min for the first 12 bottles, every 10 min for the next 8 bottles and every 20 min for the last 4 bottles. In this way, a more detailed qualitative characterization was achieved in the first part of the flow and, at the same time, an adequate description of the entire hydrograph was obtained for most events, excluding the longer ones. Ten or more samples were collected in twelve monitored rainfall events, but equipment failures or poor precipitation limited sample acquisition for other events. In total, 248 samples were analyzed.

Relevant pollution parameters were searched for in the samples, i.e., specific conductivity (SC), total suspended solids (TSS), settleable solids (SetS), biochemical oxygen demand (BOD), chemical oxygen demand (COD), lead (Pb), zinc (Zn), iron (Fe), total nitrogen (TN), total phosphorus (P) and total hydrocarbons (HC). The analyses were carried out in compliance with UNI EN ISO 9002:2004 standard in a certified laboratory (Analytica srl, Pavia, Italy).

The analysis of urban pollutant dynamics and FF phenomenon was performed for a representative subset of rainfall events (Table 1). Several requirements for event selection were implemented together:

- Absence of failures in the monitoring equipment, lost samples or problems during the laboratory analyses;
- Free-surface flow conditions in the sewerage during the transit of the wet-weather runoff;
- Rainfall depth equal or greater than 5 mm;
- Maximum rainfall intensity of at least 0.2 mm/min;
- Maximum rainfall depth over 15 min of at least 2 mm;
- Adequate sample number and distribution that allow for a comprehensive experimental characterization of the quality of the entire hydrograph.

The following quality parameters were considered: TSS, COD, BOD5, Pb, Zn, TN and P. These parameters help in describing the behavior of organic and inorganic pollution, heavy metals and nutrients during wet-weather runoff for a comprehensive investigation of urban pollutant dynamics and FF phenomenon.

Figure 3 provides a statistical description of the pollution concentrations that characterize the samples acquired for the selected events.

Table 1. Main characteristics of the selected rainfall events for the Bivio Vela catchment: d: rainfall duration; h rainfall depth; i_{max} maximum rainfall intensity; $h_{max15'}$ maximum rainfall depth over 15 min; ADP antecedent dry period; N_{CS} number of collected samples.

Event Number	d (min)	h (mm)	i_{max} (mm/min)	$h_{max15'}$ (mm)	ADP (d)	N_{CS}
1	112	6.4	0.49	1.96	1.0	19
2	140	5.6	0.42	1.68	1.2	10
3	700	70.0	3.24	24.32	9.0	16
4	2100	33.0	0.45	2.95	9.1	24
5	249	5.8	0.20	1.21	2.4	24
6	423	6.6	0.10	1.00	12.4	24
7	336	9.8	0.14	2.56	2.8	24
8	425	9.4	0.34	1.94	17.3	24

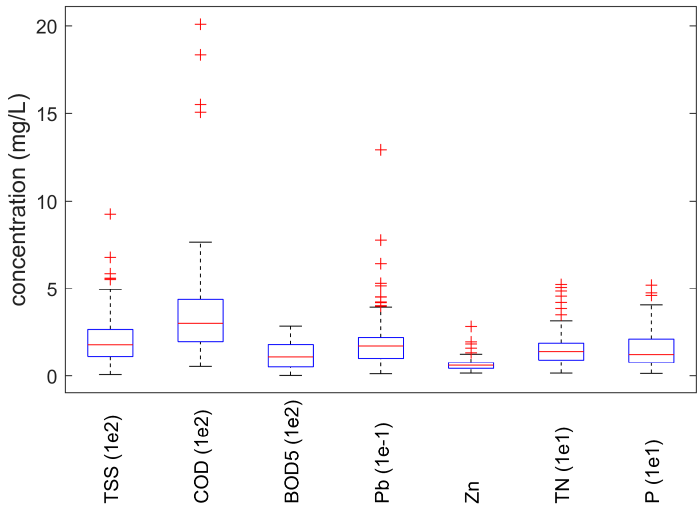

Figure 3. Summary statistics with box plots of the pollution parameters for the storms presented in Table 1. On each box, the central mark denotes the median, and the lower and upper borders of the box indicate the 25th and 75th percentiles, respectively. The whiskers extend to the most extreme data points not considered outliers, and the outliers are plotted individually using the "+" marker symbol.

2.2. Definition of Representative Pollutographs and FF Analysis

The approach described in the following section has been adopted in this work to assess the pollutant concentration modifications in water quality samples collected during each rainfall event. The runoff process related to every rainfall event is partitioned into several slices by defining an increment of runoff depth. For each one of the slices, the mean pollutant concentration (EMC) is calculated.

Due to the relative complexity of the examined drainage system, the assessment of the runoff depth at the final reach of the catchment represents a crucial aspect of the analysis. In fact, evaluating the hydrograph at the most downstream reach of the sewer system is not useful to represent the entire process of the catchment runoff. This occurs because, during wet-weather conditions, a significant percentage of the runoff pertaining to SC1 is directed to the receiving water body via the overflow structure combined with PS1. The contributive area of the runoff at the closure section of the system is therefore estimated to be equal to the sum of the impermeable surface of SC2 and a fraction, which may vary according to the considered rainfall event, of the impermeable surface of SC1. For each event, it is assumed that that the ratio between the volume sent from PS1 to SC2 and the overall incoming volume from SC1 is equal to the contributing impervious area of SC1 divided by the total impervious area of SC1. With this approach, the contributing impervious area of SC1 associated with the hydrograph at the closure section, where quality data are acquired, is identified event by event.

Once the runoff depth has been determined, a slice of runoff is set and the parameter EMC is assessed for the runoff steps considered within every event. Combining all the events sampled at the catchment, the behavior of the EMC inside every slice for each pollutant species is detected.

Following the above-mentioned approach, for every slice of runoff, a number of plausible EMC values are inferred. The non-parametric Wilcoxon rank-sum test [33] can be adopted to detect the variation in concentration values within the runoff process. Applying this test, both initial and background concentration values of the pollutants in the catchment can be detected, as well as the volume and strength of FF by grouping those slices of concentrations that are homogeneous from a statistical point of view. The fundamental stages of this method are described in Figure 4.

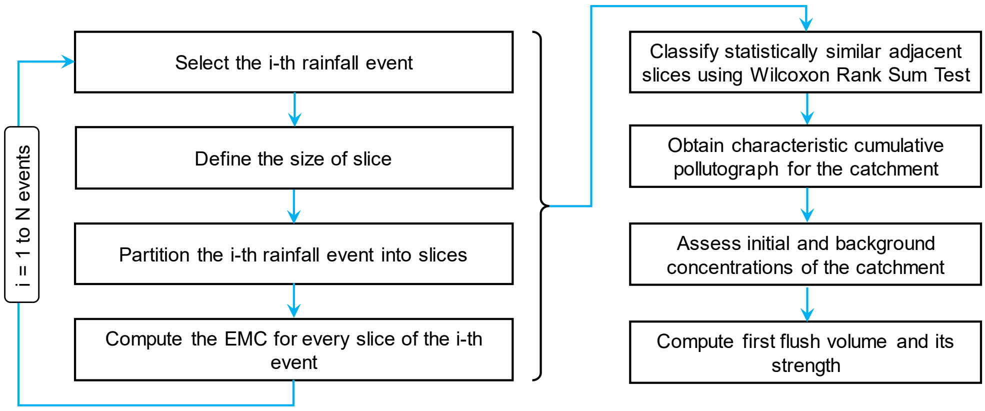

Figure 4. Flow chart of the analysis method.

Concerning the definition of the slice size, runoff values equal to 0.5–1 and 2 mm are assumed in the analysis. Adopting a base size of 1 mm allows the inclusion of at least one wet-weather sample in every slice, thus obtaining a reliable representation of the mean concentration of the pollutant in every slice. Due to the areal extension of the examined catchment, half the base size was also investigated for the slice; moreover, this option cannot guarantee obtaining at least one data sample per slice. Finally, twice the base size of the slice is considered, leading to a loss in the resolution of the time-analysis of the mean concentrations during stormwater runoff; as a consequence, a rough FF volume estimate is obtained since this volume is a multiple of the adopted slice size.

The computed value of the EMC is a flow-weighted concentration of the pollutant for each slice. The adjacent concentrations sampled at discrete time instants are linearly interpolated to obtain continuous runoff quality data. At the beginning of the runoff process, the pollutant concentrations are assumed to have the same value as that measured in the first sample; similarly, the pollutant concentrations are assumed to be constant after the last sample. The monitoring procedure and the criteria adopted to select rainfall events ensure that the time span of the sampling activity is almost coincident with the duration of every stormwater event. In this way, the first sample will be collected at or near to the beginning of the runoff, while the last is sampled close to its end.

The slices' EMCs are assessed for all the rainfall events considered, then box and wisher representations are obtained for each slice, thus obtaining quantitative information of how pollutant concentrations are distributed within every slice. The earlier slices contain a greater population of possible concentrations than the subsequent slices because the rainfall depth from each storm event is highly stochastic. When the number of EMC values for every slice is smaller than five, the statistical analysis stops.

With the non-parametric Wilcoxon rank-sum test, it is possible to evaluate whether the sets of EMC from contiguous slices are indifferent. If this happens, these slices are merged and considered as a single population compared to the one belonging to the adjacent slice. The process stops when the next consecutive slice is different from a statistical point of view. The test compares with the subsequent slice each one whose population is different to that of the previous group. Once a group of slices that are statistically indifferent has been defined, its concentration distribution is evaluated, thus leading to reorganized box and whisker plots.

The last stage of the procedure allows the detection of the first flush that takes place if all the following conditions are satisfied: the Wilcoxon rank-sum test returns multiple slices from grouping the initial ones; the median of aggregated box plots shows a declining evolution. Computing the median of the extreme groups (i.e., first and last, respectively) provides the initial concentration and the background concentration. The part of the runoff volume corresponding to the groups that precede that defining the background concentration is used to estimate the first flush volume (V_{FF}). Testing the population of the last group against that of the initial group allows one to check for the median indifference and provides the FF strength as the probability of this test ($P_{FF/BG}$).

3. Results and Discussion

The analysis carried out on the discrete experimental data in accordance with the first steps of the procedure described in the previous section provides the statistical distribution of the evolution of mean pollutant parameters in wet-weather runoff, allowing the identification of representative pollutographs for the catchment.

Figures 5 and 6 depict the distribution of EMC in each slide of runoff. Figure 5 shows the basic statistics of EMC for TSS data for slice of runoff equal to 0.5–1 and 2 mm, while Figure 6 displays the basic statistics of the EMC for all the examined parameters (except for TSS, which is presented in Figure 5) with a slice of runoff equal to 1 mm.

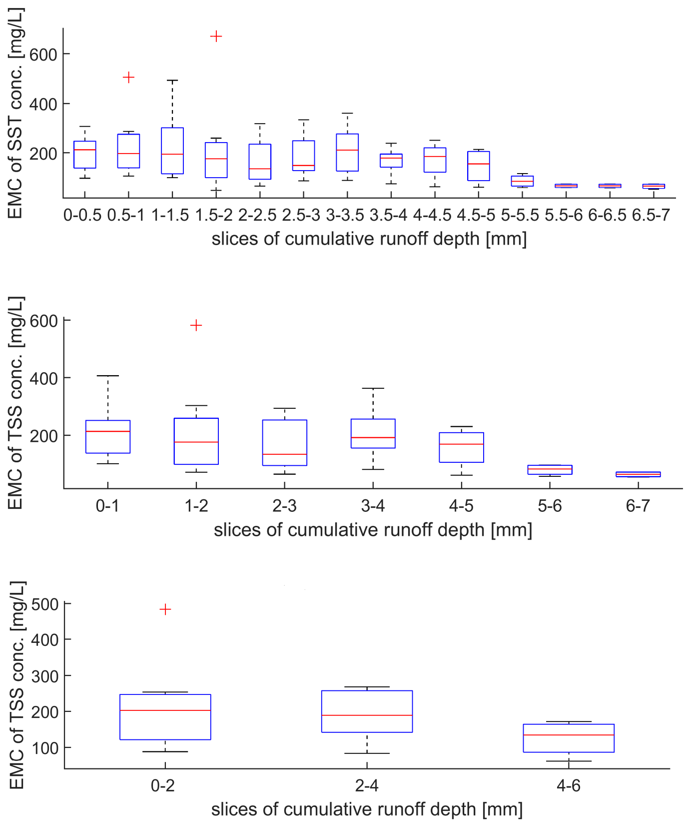

Figure 5. Summary statistics with box plots before grouping of TSS mean concentration data for a slice of runoff equal to 0.5–1 and 2 mm. On each box, the central mark denotes the median, and the lower and upper borders of the box indicate the 25th and 75th percentiles, respectively. The whiskers extend to the most extreme data points not considered outliers, and the outliers are plotted individually using the "+" marker symbol.

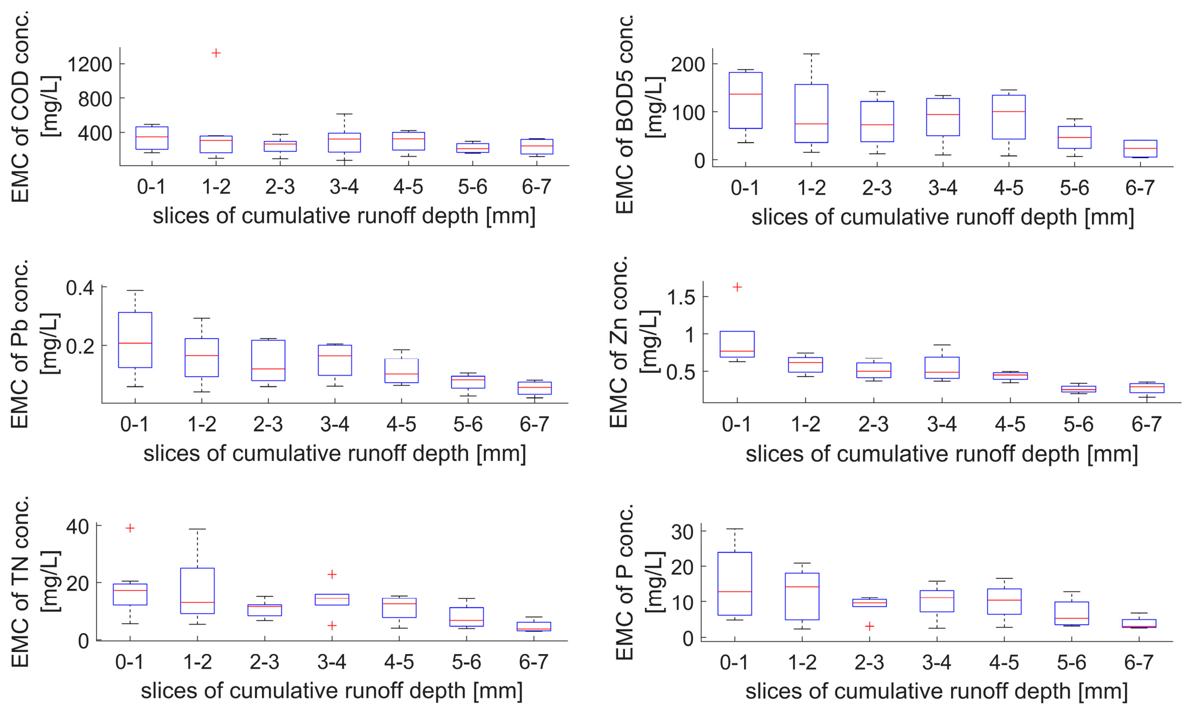

Figure 6. Summary statistics with box plots before grouping of the mean concentration data for COD, BOD5, Pb, Zn, TN, P with a slice of runoff equal to 1 mm. On each box, the central mark denotes the median, and the lower and upper borders of the box indicate the 25th and 75th percentiles, respectively. The whiskers extend to the most extreme data points not considered outliers, and the outliers are plotted individually using the "+" marker symbol.

The graphs show that the EMCs obtained in earlier slices experience higher variability than the subsequent slices of runoff, which is consistent with the observation that several factors influence the initial pollution of wet-weather runoff in an urban catchment, including the peculiar features of the precipitation event, the duration of the previous drought period and the maintenance rules for urban surfaces [28,34].

Median concentrations of the initial slices of runoff are typically greater than the subsequent median values, but the trend of median EMC is not sharply defined since an intermediate oscillatory behavior occurs for all pollutant parameters. Considering a slice of runoff equal to 2 mm the oscillatory tendency is not possible due to the coarse description of the evolution of the quality characteristics with this slice.

Figures 7 and 8 show the aggregate box plots of the EMC data after the application of the Wilcoxon rank-sum test with level of significance α equal to 0.05. Figure 7 presents the results after grouping for the TSS EMC data with slices of runoff equal to 0.5–1 and 2 mm. Figure 8 shows the graphs after grouping for all the examined pollutant parameters (except for TSS, which is presented in Figure 7) with a slice of runoff equal to 1 mm.

The results obtained for slices of runoff equal to 0.5 and 1 mm are the same for TSS concentrations, and analogous results are also found for all the examined pollutant parameters, which shows consistent grouped slices. The coarse description of the pollutant evolution with a slice size of 2 mm changes some results and leads to a unique slice group for some parameters such as TSS. Therefore, in agreement with previous findings on a catchment with a similar monitoring protocol, this slice of runoff is not recommended and it should be excluded from the analysis [25].

For a slice of 1 mm, all the examined pollutants except for COD exhibit two slice groups after grouping, allowing the detection of the first flush phenomenon. The first flush volume is equal to 5 mm for TSS and Zn, while it is 6 mm for BOD5, Pb, TN and P, highlighting the peculiar behavior of every pollutant in the urban rainfall-runoff process.

In order to test the sensitivity of the results on the adopted level of significance of the Wilcoxon rank-sum test, different levels of significance are examined up to a minimum value of 0.01. Figures 9 and 10 present the aggregate box plots of the EMC data after the application of the Wilcoxon rank-sum test with level of significance α equal to 0.01. Figure 9 presents the results after grouping for TSS EMC data with slices of runoff equal to 0.5–1 and 2 mm. Figure 10 shows the graphs after grouping for all the examined pollutant parameters (except for TSS, which is presented in Figure 9) with a slice of runoff equal to 1 mm.

The results are to some extent dependent on the significance level. By decreasing the statistical significance level from 0.05 to 0.01, more stringent rules are needed to reveal the first flush phenomenon. Excluding from the analysis the slice size of 2 mm, the first flush is detected for all the considered significance levels for TSS, Zn and TN, while other pollutants (i.e., COD, BOD5, Pb and P) do not satisfy the test requirements with a statistical significance of 0.01. This behavior is consistent with the more stringent test requirements that are associated with a lower level of significance. As the level of significance decreases, the probability increases that contiguous slices are statistically indifferent and, thus, grouped. Accordingly, for some pollutants, the number of boxes diminishes after grouping.

Tables 2 and 3 show the values of initial and background concentrations, and the detected volume of first flush for slices of runoff equal to 0.5 and 1 mm with levels of significance of 0.05 and 0.01. V_{FF} and $P_{FF/BG}$ are reported in gray color for a unique slice group after aggregation; these values correspond to those related to the lowest probability value of the Wilcoxon rank-sum test applied to the contiguous slices before grouping.

The results shows that initial concentrations tend to decrease as the level of statistical significance diminishes. Conversely, the background concentrations of some pollutants exhibit an increasing trend for decreasing significance level. This behavior is justified by the more stringent test requirements to detect differences between populations of adjacent slices when the level of significance is reduced. Accordingly, for some pollutants, the number of boxes diminishes after the test grouping.

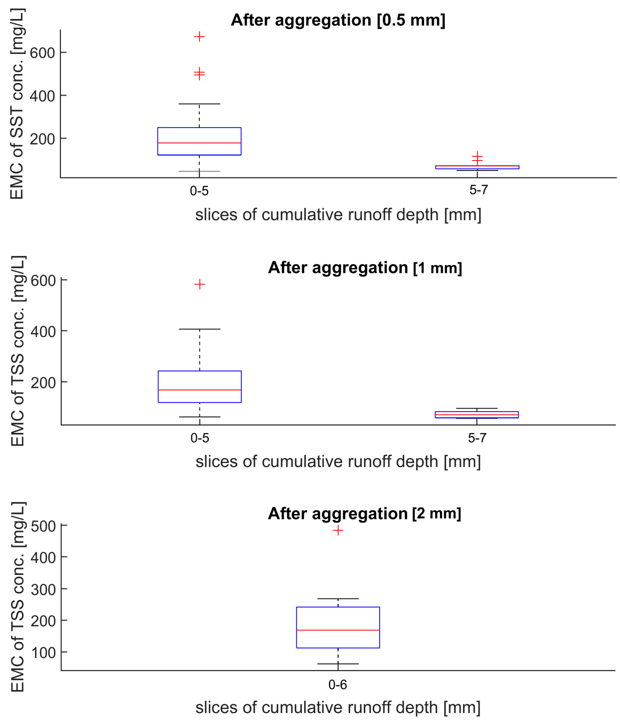

Figure 7. Summary statistics with box plots after grouping of TSS mean concentration data for slices of runoff equal to 0.5–1 and 2 mm, α = 0.05. On each box, the central mark denotes the median, and the lower and upper borders of the box indicate the 25th and 75th percentiles, respectively. The whiskers extend to the most extreme data points not considered outliers, and the outliers are plotted individually using the "+" marker symbol.

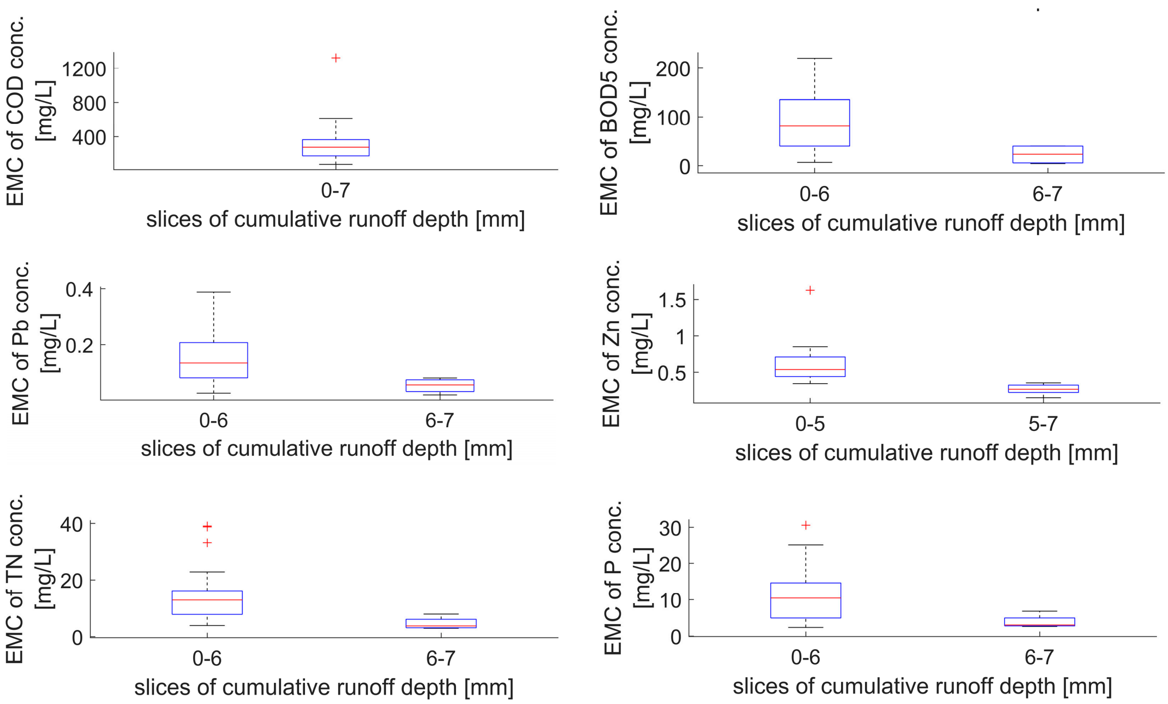

Figure 8. Summary statistics with box plots after grouping of the mean concentration data for COD, BOD5, Pb, Zn, TN, P with a slice of runoff equal to 1 mm, α = 0.05. On each box, the central mark denotes the median, and the lower and upper borders of the box indicate the 25th and 75th percentiles, respectively. The whiskers extend to the most extreme data points not considered outliers, and the outliers are plotted individually using the "+" marker symbol.

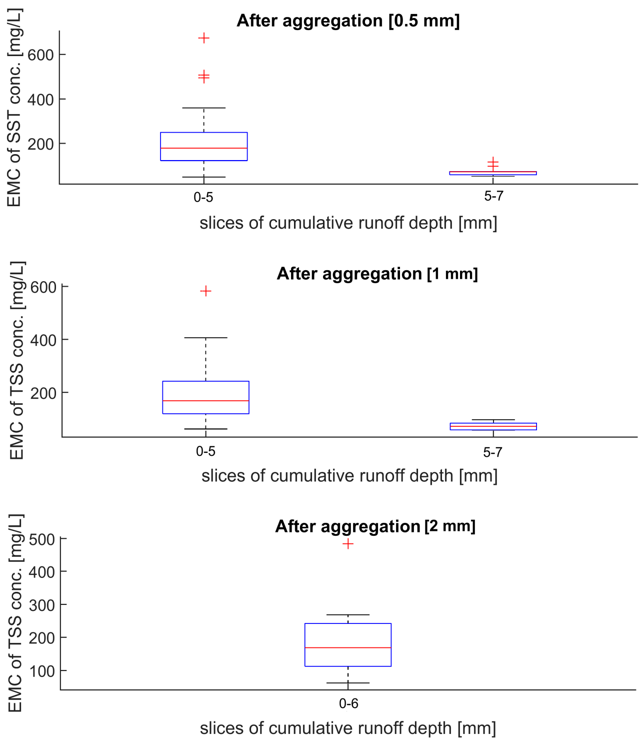

Figure 9. Summary statistics with box plots after grouping of TSS mean concentration data for slices of runoff equal to 0.5–1 and 2 mm, α = 0.01. On each box, the central mark denotes the median, and the lower and upper borders of the box indicate the 25th and 75th percentiles, respectively. The whiskers extend to the most extreme data points not considered outliers, and the outliers are plotted individually using the "+" marker symbol.

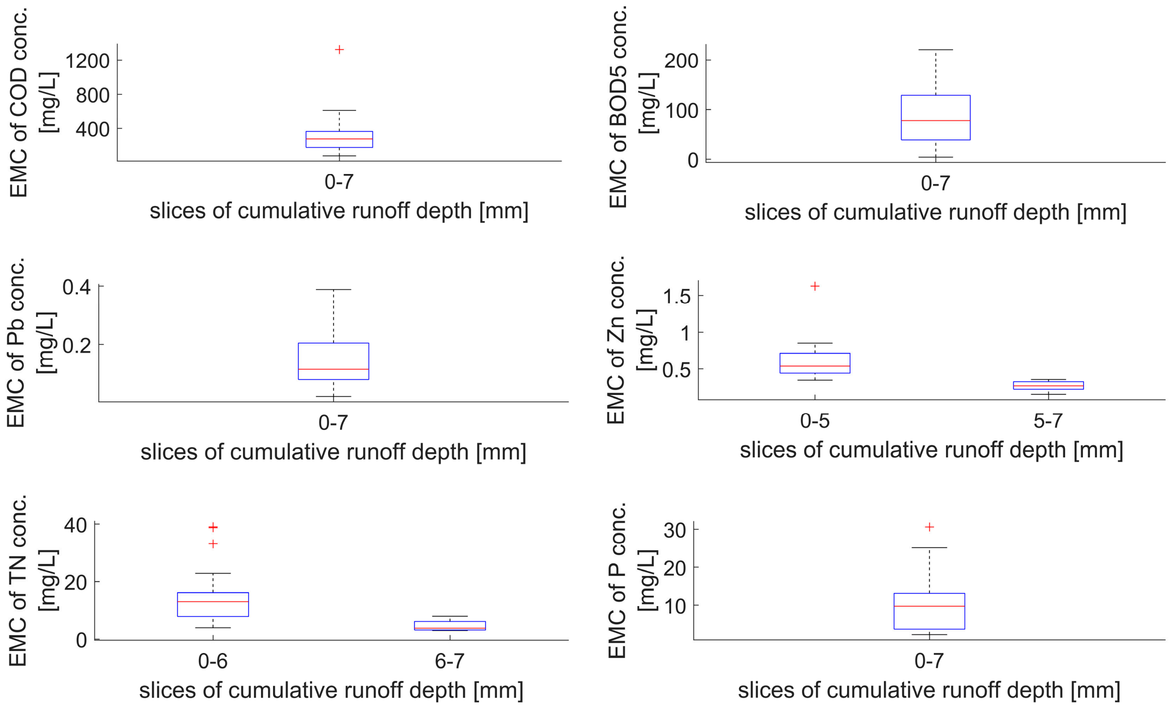

Figure 10. Summary statistics with box plots after grouping of the mean concentration data for COD, BOD5, Pb, Zn, TN, P with a slice of runoff equal 1 mm, α = 0.01. On each box, the central mark denotes the median, and the lower and upper borders of the box indicate the 25th and 75th percentiles, respectively. The whiskers extend to the most extreme data points not considered outliers, and the outliers are plotted individually using the "+" marker symbol.

Initial and background concentrations change slightly if the adopted slice of runoff decreases from 1 to 0.5 mm. These variations are comparable to the uncertainties inherent in the acquisition of experimental data. The strength of the first flush measured by $P_{FF/BG}$ varies with the slice size for every pollutant. The phenomenon is more intense and pronounced with a 0.5 mm slice than with a 1 mm slice. This result corroborates the findings of previous studies [24,25], which attribute the decrease in the strength of the phenomenon as the size of the slices increase to the "dilution effect" of the larger slices. An important finding is that V_{FF} varies within a limited range of 5–6 mm for the examined parameters with both 0.5 and 1 mm slice sizes, except for COD, which does not exhibit the FF phenomenon. The detected V_{FF} allows one to at least halve the median EMC concentration of TSS, BOD5, Pb, Zn, TN and P compared to initial values.

Table 2. Results after slice grouping with α = 0.05. N_{SG}: number of slice groups; V_{FF}: volume of first flush; C_{IN}: initial concentration; C_{BG}: background concentration; $P_{FF/BG}$: probability value of the Wilcoxon rank-sum test applied to the first and last group. V_{FF} in gray color refers to the lowest probability value of the tests; $P_{FF/BG}$ in gray color is the lowest probability value of the tests.

Slice Runoff (mm)	Parameter	N_{SG}	V_{FF} (mm)	C_{IN} (mg/L)	C_{BG} (mg/L)	$P_{FF/BG}$
0.5 mm	TSS	2	5	178.46	72.70	5.47×10^{-8}
	COD	1	2	273.40	273.40	2.92×10^{-1}
	BOD5	2	5.5	95.34	23.69	2.74×10^{-5}
	Pb	2	5.5	0.14	0.06	2.11×10^{-5}
	Zn	3	5	0.75	0.28	2.28×10^{-6}
	TN	2	5.5	13.36	4.01	2.79×10^{-6}
	P	2	5.5	10.41	2.98	2.79×10^{-6}

Table 2. *Cont.*

Slice Runoff (mm)	Parameter	N_{SG}	V_{FF} (mm)	C_{IN} (mg/L)	C_{BG} (mg/L)	$P_{FF/BG}$
1 mm	TSS	2	5	168.73	72.70	1.65×10^{-4}
	COD	1	2	277.45	277.45	2.42×10^{-1}
	BOD5	2	6	80.88	23.29	1.77×10^{-2}
	Pb	2	6	0.13	0.06	1.34×10^{-2}
	Zn	2	5	0.54	0.27	4.98×10^{-5}
	TN	2	6	12.90	3.79	6.44×10^{-3}
	P	2	6	10.41	3.04	1.89×10^{-2}

Table 3. Results after slice grouping with $\alpha = 0.01$. N_{SG}: number of slice groups; V_{FF}: volume of first flush; C_{IN}: initial concentration; C_{BG}: background concentration; $P_{FF/BG}$: probability value of the Wilcoxon rank-sum test applied to the first and last group. V_{FF} in gray color refers to the lowest probability value of the tests; $P_{FF/BG}$ in gray color is the lowest probability value of the tests.

Slice Runoff (mm)	Parameter	N_{SG}	V_{FF} (mm)	C_{IN} (mg/L)	C_{BG} (mg/L)	$P_{FF/BG}$
0.5 mm	TSS	2	5	178.5	72.7	5.47×10^{-8}
	COD	1	2	273.4	273.4	2.92×10^{-1}
	BOD5	1	5.5	70.5	70.5	1.10×10^{-2}
	Pb	2	6	0.13	0.05	6.04×10^{-4}
	Zn	2	5	0.55	0.28	1.06×10^{-8}
	TN	2	5.5	13.36	4.01	2.79×10^{-6}
	P	1	5.5	8.65	8.65	1.58×10^{-2}
1 mm	TSS	2	5	168.7	72.7	1.65×10^{-4}
	COD	1	2	277.4	277.4	2.42×10^{-1}
	BOD5	1	6	77.1	77.1	1.77×10^{-2}
	Pb	1	6	0.11	0.11	1.34×10^{-2}
	Zn	2	5	0.54	0.27	4.98×10^{-5}
	TN	2	6	12.90	3.79	6.44×10^{-3}
	P	1	6	9.73	9.73	1.89×10^{-2}

In order to test the dependence of the obtained results on the peculiarities of the case study, i.e., land use and complexity of the sewerage system, the outcomes of the procedure are compared with those obtained in a previous investigation in a neighboring residential catchment of Pavia, Cascina Scala [25].

Consistent with Table 2 for Bivio Vela, Table 4 reports the results achieved in terms of N_{SG}, V_{FF}, C_{IN}, C_{BG} and $P_{FF/BG}$ for the examined pollutants at Cascina Scala with slice sizes of 0.5 and 1 mm and a significance level of 0.05.

The Bivio Vela industrial catchment exhibits a lower number of slice groups and less relevant differences between initial and background concentrations for all the examined pollutants compared to the case of the residential catchment of Cascina Scala. C_{IN} are higher at the Cascina Scala catchment (except for P), while background values are often greater at the Bivio Vela catchment, and this is consistent with the lower number of slices after grouping at the Bivio Vela catchment. The strength of the FF is comparable for the two catchments (except for COD, which does not exhibit FF at Bivio Vela catchment), with a confirmed decreasing trend of $P_{FF/BG}$ for decreasing slice size of runoff. A relevant difference that emerges from the comparison is the wider range of the V_{FF} for the examined pollutants at the Cascina Scala catchment. This result is of particular interest since both catchments are located in Pavia, northern Italy, thus exhibiting the same climatic features and precipitation characteristics. Also, the adopted monitoring equipment and sampling protocol are similar for the two catchments. The different outcomes obtained from comparing the two databases are likely attributable to the different characteristics (extension and land use) of the two catchments and to the relative complexity of the sewerage system.

Table 4. Results after slice grouping applied to Cascina Scala database for TSS, COD, Pb, Zn, TN and P with $\alpha = 0.05$. N_{SG}: number of slice groups; V_{FF}: volume of first flush; C_{IN}: initial concentration; C_{BG}: background concentration; $P_{FF/BG}$: probability value of the Wilcoxon rank-sum test applied to the first and last group.

Slice Runoff (mm)	Parameter	N_{SG}	V_{FF} (mm)	C_{IN} (mg/L)	C_{BG} (mg/L)	$P_{FF/BG}$
0.5 mm	TSS	3	6	709.6	75.5	1.3×10^{-4}
	COD	3	2.5	1132.4	131.0	1.1×10^{-8}
	Pb	2	1	0.27	0.06	6.9×10^{-7}
	Zn	2	5	0.33	0.19	1.1×10^{-5}
	TN	2	2.5	23.19	7.96	1.9×10^{-4}
	P	3	3	5.62	1.07	4.9×10^{-8}
1 mm	TSS	3	6	786.0	60.5	2.9×10^{-3}
	COD	4	6	1122.3	57.7	4.0×10^{-3}
	Pb	2	1	0.32	0.06	1.6×10^{-3}
	Zn	2	5	0.32	0.17	2.8×10^{-3}
	TN	2	2	25.02	8.45	5.3×10^{-3}
	P	3	3	5.63	1.02	8.6×10^{-5}

The Cascina Scala catchment has a smaller surface area, and a shorter and less complex urban drainage system compared to the Bivio Vela catchment. Smaller surface area and simpler system structure fosters a smoother decreasing trend of the mean pollutant concentrations during the evolution of the runoff at Cascina Scala compared to the Bivio Vela catchment.

Hydrographs and pollutographs at the final reach of Bivio Vela are the sum of the contributions from the two sub-catchments, SC1 and SC2, which correlate with a difference in time lag. Furthermore, in wet weather, a relevant part of the incoming flow rate from SC1 is discharged into the receiving water course through CSO1. The time lag between the hydrographs of the two sub-catchments (partial hydrograph for SC1 and total hydrograph for SC2) is likely the main reason for the oscillatory behavior of median EMC, which occurs for all pollutant parameters for the intermediate slices of runoff (Figures 5 and 6). The FF phenomenon is still present, and it is likely supported by the fact that only a part of the hydrograph from SC1 correlates with the final hydrograph.

The different land use types of the two experimental catchments also affect the results, as can be observed from the markedly different initial values of concentrations, e.g., for slice size 1 mm and $\alpha = 0.05$, C_{IN} of TSS is 786.0 mg/L at the Cascina Scala catchment and 168.73 mg/L at the Bivio Vela catchment; C_{IN} of COD is 1122.3 mg/L at the Cascina Scala catchment and 277.45 mg/L at the Bivio Vela catchment. These results highlight significantly higher initial levels of these parameters in the residential catchment compared to the industrial one. Cascina Scala as well as Bivio Vela exhibits a wider distribution of EMC in initial than in final aggregate slice since many factors affect the initial pollution of urban stormwater runoff, such as intensity of rainfall, antecedent dry period and frequency of cleaning operations on urban surfaces [20,35]. Also, background concentrations assume peculiar values, which are representative of each catchment feature, although the final values for the two databases are not too dissimilar.

Despite the wider range for V_{FF}, the results of the Cascina Scala catchment confirm that a runoff depth of 6 mm allows a reduction in the catchment's stormwater pollutant concentrations to background levels for all the examined parameters. This value, which allows background pollution levels from both examined databases of Pavia to be obtained, seems fairly consistent with the design criteria imposed by the Lombardy region in Italy for wet-weather detention tanks. Regional Regulation of Lombardy Region n. 6/2019 imposes a reference storage capacity of 50 m^3 per contributing impervious hectare, i.e., 5 mm of runoff depth. The stormwater volume stored in each event should be conveyed at the treatment facility within 48 h from the end of stormwater runoff in the sewerage.

The detected V_{FF} volume should represent an overall reference value, guiding environmentally sustainable decisions for effective design and management of stormwater control and treatment practices.

4. Conclusions

In this article, a sound innovative analysis was carried out on selected experimental data on wet-weather runoff from an industrial catchment of northern Italy. The procedure provided the statistical characterization of the evolution of mean pollution parameters in subsequent slices of runoff, allowing the recognition of representative pollutographs for the catchment. Systematic grouping of adjacent slices through the Wilcoxon rank-sum test allowed the assessment of the volume of first flush needed to reduce stormwater pollutant concentrations to the catchment's background levels, accounting for the dynamics of different pollutant types. The achieved volume of first flush as well as the attained representative initial and background concentrations were to some degree dependent on the chosen level of significance and were quite consistent for a slice of runoff up to 1 mm, while a wider slice led to an overly coarse and inaccurate analysis of the evolution of runoff quality characteristics. The peculiarities of the catchment affected the outcomes of the procedure since surface extension, land use and complexity of the sewerage system were the main reasons for the different results for the two neighboring urban catchments affected by the same climatic features and rainfall conditions.

The adopted reliable assessment of first flush volume and strength is useful to guide environmental sustainable decisions that address the design and management of stormwater control and treatment practices. The analysis provides the runoff depth that must be captured to reach background concentrations, and it also allows the detection of representative pollutographs to be adopted for studies on the performance assessment of solutions aimed at the environmental sustainability and safeguarding of natural resources. Similarly, the results of the procedure applied to databases from catchments located in the Lombardy region allowed a critical evaluation of the effectiveness of rules imposed by the current Regional Regulation on environmental protection. The advantages of the analysis methodology and the relevance of the obtained results promote the application of this methodological approach for other case studies, focusing on the implications for stormwater management practices, particularly for the effective design of control and treatment systems. The modifications of the catchment's representative evolution of mean pollution concentrations and first flush outcomes will be investigated in future research to account for the modification of rainstorm patterns due to climate change. The results of these further investigations will be published in due course.

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