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Analysis of Surrogate Physicochemical Parameters for Studying Heavy Metal Pollution in Urban Road Runoff

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Abstract: The pollution associated with road runoff water can generate significant impacts on the receiving natural environment due to the significant masses mobilized under certain climate, morphological, and anthropic conditions. The aim of this paper is to show an analysis of the possible surrogate conventional physicochemical parameters of pollution by heavy metals (HMs) in urban road runoff. The best surrogate physicochemical parameters are detected by a differentiated analysis between the HM concentrations (Fe, Al, As, Ba, Cd, Co, Cu, Cr, Mn, Hg, Ni, Pb, V, and Zn) in the total, particulate, and dissolved fractions. This analysis is also performed under two scenarios of runoff event energy according to the mobilized TSS load. The results suggested that it was easier to detect surrogate parameters for total HM concentrations during higher-energy runoff events. The outcomes hinted that regardless of the runoff event energy, it was easier to detect conventional surrogate parameters for the particulate HM concentration compared to the dissolved HM concentration. The findings showed for total HM concentration that the best surrogate parameter during higher-energy runoff events was TSS. The best surrogate HM during these runoff events was Fe. The results also suggested that HMs with high percentages of association with the particulate fraction (>70%) of road runoff were the best surrogates for the other HMs under study. For lower-energy runoff events, the best surrogate parameter was VSS, although TSS also showed good behavior.

Keywords: heavy metal; road runoff; urban pollution; surrogate parameter; water quality

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1. Introduction

Experience in pollution management has shown a direct relationship between urban growth and pollutant loads discharged into drainage systems and water bodies, soil, and atmosphere [1]. The pollution associated with road runoff water can generate significant impacts on the receiving natural environment due to the important masses mobilized under certain climate, basin morphological, and anthropic conditions [2]. Worldwide, concern is reported about urban pollution with heavy metals (HMs) due to their continuous emission, long periods of residence, transport within air masses, their eventual deposition on the surface, and that these are significantly mobile and potentially bioavailable [3–5]. Road surfaces represent only part of the urban landscape, but their high degree of impermeability favors their contribution with significant HM loads during runoff events [6,7].

Currently in the European Union, according to the Water Framework Directive—2000/60/EC [8], it is established, for example, that surface runoff from airports, transport roads, urban areas, industrial areas, and gas stations are part of the diffuse pollution sources. These runoffs should be considered as pressures that put at risk the good status of water bodies and generate non-compliance with urban environmental quality guidelines. The scarcity of specific regulations in the Spanish State and developing countries in terms of HMs in urban road runoff, makes it necessary to advance in this type of studies to look for possible surrogate physicochemical parameters that allow indicating the presence of HMs in road runoff. These studies of surrogate parameter detection are useful to evaluate a possible reduction in the monitoring costs associated with the surveillance and control of HMs. These studies are also relevant because from their findings, guidelines can be suggested to unify the criteria for the assessment of impact risks on receiving water bodies in urban environments. There are different guidelines for the runoff pollution control in water bodies that have as their only control criterion the total suspended solid (TSS) concentration. For example, this occurs in the design and operation of sustainable urban drainage systems—SUDS [9,10]. Thus, it is also relevant to conduct studies that focus on evaluating the adequate performance of TSS as a surrogate parameter for HMs in road runoff waters. Likewise, with this type of studies, surrogate parameters additional to TSS or a surrogate HM to those reported in road runoff water could be detected. All the above makes this study have a certain degree of novelty compared to those carried out so far.

Most of the pollutants that accumulate on the urban road surface are of anthropogenic origin and can come from different emission sources, usually continuously, and distributed along the road [11]. Occasionally, there are also specific pollution sources due to accidental spills, for example, of agricultural, chemicals, and petroleum products, due to traffic accidents [12]. Several authors have sought the origin of HMs in road environments, relating them to the different parts of vehicles and the elements of highways and roads, and their operation [13]. The HM contribution by vehicles on road surfaces is due to fuel and lubricant leaks, body rust, tire and brake wear, and combustion gases [14,15]. The predominant HMs in urban road runoff are Zn, Pb, and Cu [16], though Fe, Ni, Hg, Cr, and Cd can also be found [17]. Differences in the different types of vehicles, fuels used, and even the pavement typology can generate variations in the HMs present in urban road runoff [18,19].

The association between runoff water quality and pollution present in sediments accumulated in dry weather on road surfaces is evident [15]. Thus, it is very likely that the factors influencing the processes of HM accumulation and washing contained in road sediments are also relevant for the study of their presence in road runoff [20]. These processes are also relevant for the identification surrogate parameters of HMs in road runoff. Commonly reported influencing factors are the following [21]: rainfall intensity, antecedent dry period, particle size, vehicles, and land use. Two mechanisms influence road sediment wash-off during rainfall events. The first is related to the material in particulate form, which detaches as a result of the direct impact of rainfall [22]. The second is related to the dissolved fraction, which dissolves, and due to its subsequent removal, becomes turbulent, favoring road sediment transport and mixture/leaching [23]. Studies on the wash-off phenomenon of HMs caused by road runoff have shown that rainfall intensity and antecedent dry period are the leading climate factors (e.g., [14,24–26]). Road sediment transport caused by runoff (wash-off) increases with rainfall intensity [27,28] and longer antecedent dry periods [29]. In addition to causing road sediment transport, runoff leads to leaching, which must be considered when analyzing the wash-off phenomenon. Ellis and Revitt [30] studied the effects of leaching on road sediment and reported the following sequence: Cd > Zn—Cu > Pb. These researchers reported that the leaching test allowed the simulation of turbulent runoff conditions on road sediment during storm drainage from the roadside surface. Stone and Marsalek [31] obtained a similar sequence for leaching tests on road sediment: Cd—Cu > Zn > Pb. These findings have led researchers to suggest that road sediment acts as an effective sink for Pb but not Cd or Cu. Nevertheless, dissolved organic matter and pH are the most important solution parameters affecting the HM mobility from road sediments [32].

The aim of this paper is to show an analysis of the possible surrogate conventional physicochemical parameters of pollution by HMs in urban road runoff. The best surrogate physicochemical parameters are detected by a differentiated analysis between the HM concentrations in the total, particulate, and dissolved fractions of road runoff. This analysis is also performed under two scenarios of runoff events (higher and lower energy) according to the mobilized TSS load. Namely, the influence of rainfall during the identification of surrogate parameters is studied. Regression models are developed between the concentrations of surrogate physicochemical parameters and HMs under study. This study is relevant because it will allow in road runoff waters (i) to detect conventional physicochemical parameters for the HM indication, (ii) to forecast their concentrations and masses mobilized from conventional water quality parameters, and (iii) to reduce the costs associated with the HM monitoring.

2. Materials and Methods

2.1. Study Site

The pilot basin characterized in this study is formed, for the most part, by the roadway of the N-651 national highway, as it passes through the town of San Valentín, in the municipality of Fene (A Coruña) in northwestern Spain (43°28′33.9′′ N; 8°10′26.2′′ W). It has a drainage network for rainwater that flows directly into a coastal water body (Ferrol estuary), which belongs to the Atlantic Ocean. The study road is two-way, with two lanes for each, and has a rolling surface of asphalt. The road is low slope, and has sidewalks, curb, and side parking areas (Figure 1). On average, annual daily traffic intensity is 17,749 vehicles, with a percentage of heavy vehicles of 1.98%. The annual rainfall at the study site is 1468 mm, which is distributed over 130 rainy days per year.

Figure 1. Road surface and adjacent areas of the study basin in Fene (A Coruña, Spain). Study basin marked in blue and green.

The area of the entire pilot basin is 48,532 m^2 (green and blue in Figure 1) and consists mainly of the highway (green), accesses to it from the shipyards and A Xunqueira Sports Center, and a small part of the urban industry. The contribution area that corresponds to the highway is 17,060 m^2, which is 35.2% of the total pilot basin. The drainage network consists of about 2 km of collectors, mostly 400 mm concrete pipe. The largest diameter present is 600 mm, in some small final stretch. The average slope of the drainage network is high, about 3.49%, which facilitate significant flow rates. A high degree of waterproofing and the small relative size of the basin gives a very low concentration time (<15 min) in the control section (Flowmeter in Figure 1). Namely, while rain events occur, the flow in the control section also occurs. The surface coverages detected in the study basin were as follows: permeable (grass, gardens, and trees = 28.8%) and impermeable (highway and roads = 71.2%). The average runoff coefficients for permeable and impermeable areas were 0.25 and 0.90, respectively. Thus, the weighted average runoff coefficient was 0.71 for the entire study basin.

2.2. Sampling System

The sampling system was structured to collect information about the HM content in runoff of the road basin under study. Thus, a runoff flow control section was set up in the lower part of the basin (flowmeter in Figure 1). This control section was in one of the manholes of storm drainage network (final section), before discharge over an estuary. The equipment installed in the control section were the following: stainless steel house (0.76 × 0.76 × 1.50 m), speed and depth Doppler sensor, ultrasonic flowmeter (HACH SIGMA 950, Darmstadt, Germany) for speed and depth Doppler sensor, suction device attached to Teflon tube (Ø 12 mm, connected to the sampling), automatic sampling (SIGMA 900, Darmstadt, Germany) of 24 bottles of 1 L each, 3 power batteries of 12 V (74 Ah) each, and a communication system by General Packet Radio Service—GPRS. The sampling period lasted 15 months (1 March 2010–30 June 2011). Flow, velocity, and depth records were taken every 5 min during the sampling period.

The collection time interval for automatic sampling (SIGMA 900, Darmstadt, Germany) was programmed considering the following factors: volumetric capacity (24 bottles of 1 L), sampled pollution parameters (sample volume needed), hydraulic behavior of the basin (concentration time < 5 min), and hydraulic conditions of the control section (water level of the events). Thus, a sampling interval of 5 min was established from the start of the respective runoff hydrograms. Table 1 shows the pollution parameters considered in this study. A total of 76 data were collected for each study variable. Lastly, rainfall information was collected by installing a seesaw rainfall gauge, located on the roof of a nearby sports coliseum (rainfall gauge in Figure 1). The rainfall gauge was located at 125 m from the study road basin (control section) and had a sensitivity of 0.20 mm per rollover. Rainfall intensity was determined for 5-min intervals. During the study period, 10 rainfall events were observed (Table 2).

Table 1. Runoff water pollution parameters considered.

Conventional Physicochemical			**HMs**		
Parameter	**Symbol**	**Unit**	**Parameter**	**Symbol**	**Unit**
Chemical oxygen demand	COD	mg/L	Aluminum	Al	mg/L
Chemical oxygen demand—Soluble	CODs	mg/L	Arsenic	As	µg/L
Biological oxygen demand (5 d)	BOD_5	mg/L	Barium	Ba	µg/L
Total nitrogen	TN	mg/L	Boron	B	µg/L
Total phosphorus	TP	mg/L	Cadmium	Cd	µg/L
Total solids	TS	mg/L	Cobalt	Co	µg/L
Suspended solids	SS	mg/L	Copper	Cu	µg/L
Volatile suspended solids	VSS	mg/L	Chromium	Cr	µg/L
Dissolved suspended solids	DSS	mg/L	Iron	Fe	mg/L
Volatile dissolved suspended solids	VDSS	mg/L	Manganese	Mn	µg/L
Total suspended solids	TSS	mg/L	Mercury	Hg	µg/L
Volatile total suspended solids	VTSS	mg/L	Nickel	Ni	µg/L
Turbidity	TUR	NTU	Lead	Pb	µg/L
Conductivity	CON	µS/cm	Vanadium	V	µg/L
pH	pH	Units	Zinc	Zn	µg/L

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

Events	01	02	03	04	05	06	07	08	09	10
DTSP (days)	0.33	17.2	0.45	0.88	5.42	15.1	11.5	8.02	14.1	21.6
Event duration (days)	1.99	0.250	0.076	0.125	0.076	0.076	0.076	0.076	0.431	0.076
Qmax (L/s)	61.1	3.22	31.1	16.2	4.64	8.63	7.76	81.0	132.1	357.9
Qmed (L/s)	5.64	1.20	4.98	2.38	0.94	1.11	1.55	9.71	5.14	37.0
Vol (m^3)	97.8	11.5	54.9	18.4	10.7	17.1	18.9	91.0	432.4	696.4
P_{total} (mm)	12.6	6.20	8.00	3.20	4.00	6.40	3.60	9.20	14.4	22.2
P_{5max} (mm)	1.00	0.60	2.20	1.00	0.40	0.40	0.20	1.80	1.60	5.80
I_{5max} (mm)/h	12.0	7.20	26.4	12.0	4.80	4.80	2.40	21.6	19.2	69.6
I_{media} (mm/h)	0.26	1.03	4.36	1.07	2.18	3.49	1.96	5.02	1.39	12.1

Note: DTSP = Antecedent dry period, Qmax = Maximum flow rate, Qmed = Average flow rate, Vol = Runoff volume, P_{total} = Total rainfall, P_{5max} = Maximum rainfall in 5 min, I_{5max} = Maximum rainfall intensity in 5 min, and I_{media} = Average rainfall intensity.

2.3. Laboratory Analysis

The following standards were considered to perform laboratory analyses of each of the parameters considered. COD: ISO 15705 [33]; CODs: ISO 15705 [33]; BOD_5: ISO 9408 [33]; TN: ISO 11905-1 [33]; TP: ISO 6878 [33]; TS: Standard Method 2540 B [34]; SS: Standard Method 2540 D [34]; VSS: Standard Method 2540 E [34]; DSS: Standard Method 2540 C [34]; VDSS: Standard Method 2540 E [34]; TSS: Standard Method 2540 B [34]; VTSS: Standard Method 2540 E [34]; pH: Standard Method 4500—H + B [34]; HMs: Standard Method 3125, Mass spectrometry with an inductively coupled plasma source [34].

2.4. Information Analysis

Hydrograms and pollutograms were determined for each of the 10 rainfall/runoff events. This in relation to each of the water quality parameters considered in this study (Table 1). The hydrograms were obtained from the flowmeter records in the control section and the pollutograms were determined from the results of the laboratory analysis performed on the samples [35]. Subsequently, the respective flowgrams were constructed for each water quality parameter considered (mass per unit of time) [35]. The parameterization of road runoff events was performed from the calculation of the event mean concentration (EMC) and site mean concentration (SMC). The EMC referred to the entire event without considering the phenomena that occurred during its development, such as the first wash phenomenon [36]. The SMC was a characteristic concentration of the pollution degree of road runoff in the study road basin [36]. Based on EMC and SMC, a comparative analysis was performed in relation to the guidelines established by Caltrans [37], Ellis and Mitchell [38], and National Stormwater Quality Database—NSQD [39]. This comparative analysis was performed for the total fraction of the road runoff.

In this study, three scenarios of information analysis were established from the observed concentrations (total, particulate, and dissolved fraction) of the parameters under study during each runoff event: (i) all observed concentrations, (ii) concentrations observed above the TSS median, and (iii) concentrations observed below the TSS median. The last two scenarios were established to differentiate higher-energy and lower-energy runoff events, respectively, in relation to the mobilized TSS load during runoff events [40]. These three scenarios were established to analyze the relationships between conventional water quality parameters and HMs under the fractions considered. Normality in the data series for each study variable was assessed using the Kolmogorov–Smirnov test (p-value > 0.05) [41]. Subsequently, through a principal component analysis (PCA) [42] and Pearson correlation [43], possible conventional water quality parameters for the HM indication in road runoff were detected (surrogate parameters). The PCA considered three steps: (i) standardization of measurements to ensure that they had the same weight in the analysis by automatically scaling the data to produce new variables, where the mean was equal to zero and the standard deviation was equal to the unit, (ii) calculation of the covariance matrix by identifying the eigenvalues and their corresponding eigenvectors, and (iii) the elimination of components that represent only a small proportion of the variation in the datasets [42]. Only principal components with eigenvalues greater than one were retained for further analysis. The retained principal components were not subjected to any rotation. The information analysis with PCA considered two phases. In the first phase, all study parameters (conventional and HMs) were considered, and in the second phase, only the two main surrogate parameters detected (conventional) and all HMs under study were considered. Linear regression models were also developed [44] to forecast the HM concentrations from the identified surrogate parameters. This was done for the three established analysis scenarios. Cumulative probability distribution graphs [45] were developed to study the variation of observed and predicted HM concentrations from the surrogate parameters. The influence of rainfall events during the identification of surrogate parameters was analyzed. During this analysis, the rainfall height and intensity [46] were considered. All statistical analyses were performed with 95% confidence and using IBM-SPSS V.19 software.

3. Results and Discussion

3.1. Water Quality and TSS Content

The MSCs observed in road runoff for the conventional parameters and HMs were compared with the following reference studies: Stockholm Water and Waste Company in Sweden [47], California Department of Transportation—CALTRANS—in the USA [48], and the database and recommended values for strategic planning models developed by Ellis and Mitchell [38]. In this comparative analysis, only the parameters reported by the reference studies were considered (Table 3). The results showed that there were conventional water quality parameters and HMs that exceeded the reference concentrations reported in road runoff. When considering mean site concentrations (MSC1), it was observed that 61.5% of the selected parameters exceeded the concentrations of at least one of the reference studies. However, when considering the median site concentrations (MSC2), it was evident that only 30.8% of the selected parameters exceeded the reference concentrations. These differences between MSC1 and MSC2 suggested the occurrence of atypical road runoff pollution events during the study period. For example, it was observed that the range of TSS concentration in road runoff during the 10 rainfall events was between 21.9–987 mg/L. This trend was also observed in the HMs under study. For example, the range of total concentration of Fe, Al, and Zn was between 660—17,130 µg/L, 490–10,860 µg/L, and 83.9–384 µg/L, respectively. The concentration range of conventional parameters and HMs considered was comparatively related to the range of rainfall intensity (1.0 mm/h–8.4 mm/h) and runoff flows (92.7–400 L/s) observed. In relation to HMs, it was observed that 37.5% of these exceeded the concentrations of at least one of the reference studies.

Additionally, a comparative analysis was performed with the HM concentrations reported by Huber et al. [22]. This was performed for an average daily traffic between 5000–15,000 vehicles/day. These researchers reviewed and analyzed HM concentration databases from 294 monitoring sites spread across six continents (Africa, Asia, Australia, Europe, and North and South America). The results showed comparatively that the total HM concentrations were between low and medium in relation to the values reported by the reference study (Table 4). Dissolved HM concentrations showed a similar trend, between low and medium.

Except for Ni, where observed concentrations were high. Overall, HM concentrations observed were between low and medium. The decreasing order in total HM concentrations was as follows (mean): Fe > Al > Zn > Ba > Mn > Cu > B > Pb > V > Cr > Ni > As > Co. In the dissolved fraction the decreasing order was as follows: Fe > Al > Ba > Zn > Mn > B > Cu > As > Ni > Cr > Co > Pb > V. Thus, the results suggested Fe, Al, and Zn as the HMs with the highest total concentrations and Ni, As, and Co as the HMs with the lowest total concentrations. Dupuis [49], Bakr et al. [50], and CALTRANS [37] reported similar results. These researchers also reported Fe, Al, and Zn as those HMs with the highest total concentrations in road runoff. Kayhanian et al. [51] also reported Fe and Al as those HMs with higher concentrations in road runoff.

Table 3. Comparison of concentrations observed in road runoff with reference studies.

Parameter	Stockholm Vatten [47]		CALTRANS [48]			Ellis and Mitchell [38]			In This Study	
	Low	**High**	**Min.**	**Max.**	**Mean**	**1st Quartile**	**3rd Quartile**	**Mean**	**SMC1**	**SMC2**
COD (mg/L)	25.0	60.0	10.0	390	118	89.1	209	137	177	74.4
TDS (mg/L)	-	-	14.0	470	109	-	-	-	84.9	76.9
TSS (mg/L)	<50.0	>175	3.00	4800	158	101	361	191	234	84.0
TN (mg/L)	<1.25	>5.00	-	-	4.80	1.50	3.70	2.40	3.90	2.70
TP (mg/L)	<0.10	>0.20	0.10	10.0	0.30	0.10	0.30	0.20	0.70	0.40
Al (μg/L)	-	-	29.0	12,600	2610	-	-	-	3480	2380
As (μg/L)	-	-	1.00	17.0	2.50	-	-	-	5.90	4.40
Cr (μg/L)	<15.0	>75.0	1.00	100	10.9	6.20	22.2	11.7	8.10	4.80
Cu (μg/L)	<9.00	>45.0	1.00	800	48.5	43.2	150	80.3	55.1	43.9
Fe (μg/L)	-	-	4100	24,000	4284	1370	7280	3160	5650	3860
Ni (μg/L)	<45.0	>225	0.90	317	12.6	7.90	51.8	20.2	7.40	4.60
Pb (μg/L)	<3.00	>15.0	1.00	2300	114	154	473	270	17.5	9.60
Zn (μg/L)	<60.0	>300	5.00	2400	228	151	752	337	173	108

Note: Bold = Higher concentrations than those reported by reference studies. Min. = Minimum, Max. = Maximum, MSC1 = Mean of MSCs, and MSC2 = Median of MSCs. The HM concentrations correspond to the total fraction.

The results showed that the mean TSS concentration (MSC1) exceeded at least one of the reference studies and the median TSS concentration (MSC2) was below all reference studies (Table 3). The findings suggested that TSS concentrations observed during runoff events ranged from low to medium. On average, for all rainfall and runoff events, the findings showed a very strong direct linear correlation between the maximum rainfall intensity (Imax. in mm/minute) and the maximum runoff flows (Qmax. in L/s) observed ($\text{Qmax.} = 62.5 \times \text{Imax.} - 23.5$, $R^2 = 0.889$). Moreover, the results showed a very strong direct linear correlation between the maximum rainfall intensity and the mean TSS loads mobilized ($\text{TSS} = 22 \times \text{Imax.} - 15.9$, $R^2 = 0.923$, TSS in mg/min). Therefore, the findings suggested TSS as the conventional water quality parameter best associated with the climate component of runoff events (i.e., rainfall intensity and runoff flow). TSS was selected to classify the energy of the observed runoff events from their median concentration during the study period: TSS concentration > median = Higher energy event and TSS concentration < median = Lower energy event. Piro and Carbone [52] also reported a significant linear correlation between runoff flow and mean TSS loads mobilized during runoff events.

Table 4. Comparison of observed HM concentrations with those reported by Huber et al. [22].

	Huber et al. [22]			**This Study**				
Total concentrations								
HMs	Min.	Mean	Max.	Median	SMC1	Evaluation	SMC2	Evaluation
Pb	3.70	32.3	136	20.3	17.5	Medium	9.60	Low
Zn	23.0	285	1000	274	173	Medium	108	Low
Ni	3.80	16.3	35.0	17.0	7.40	Low	4.60	Low
Cu	7.00	64.6	280	30.5	55.1	Medium	43.9	Medium
Cr	2.00	12.0	24.2	9.90	8.10	Medium	4.80	Low
Dissolved concentrations								
HMs	Min.	Mean	Max.	Median	SMC1	Evaluation	SMC2	Evaluation
Pb	0.13	0.90	2.80	0.40	0.20	Low	0.10	Low
Zn	7.90	68.0	258	31.0	37.4	Medium	32.3	Low
Ni	0.50	0.90	1.30	1.00	1.30	High	1.40	High
Cu	2.70	16.0	65.0	11.2	15.9	Medium	12.4	Medium
Cr	0.60	1.20	1.80	1.20	0.40	Low	0.50	Low

Note: Evaluation: low, $< \left(\overline{X} - \frac{X}{2}\right)$; medium, between $\left(\overline{X} - \frac{X}{2}\right)$ and $\left(\overline{X} + \frac{X}{2}\right)$; high, $> \left(\overline{X} + \frac{X}{2}\right)$.

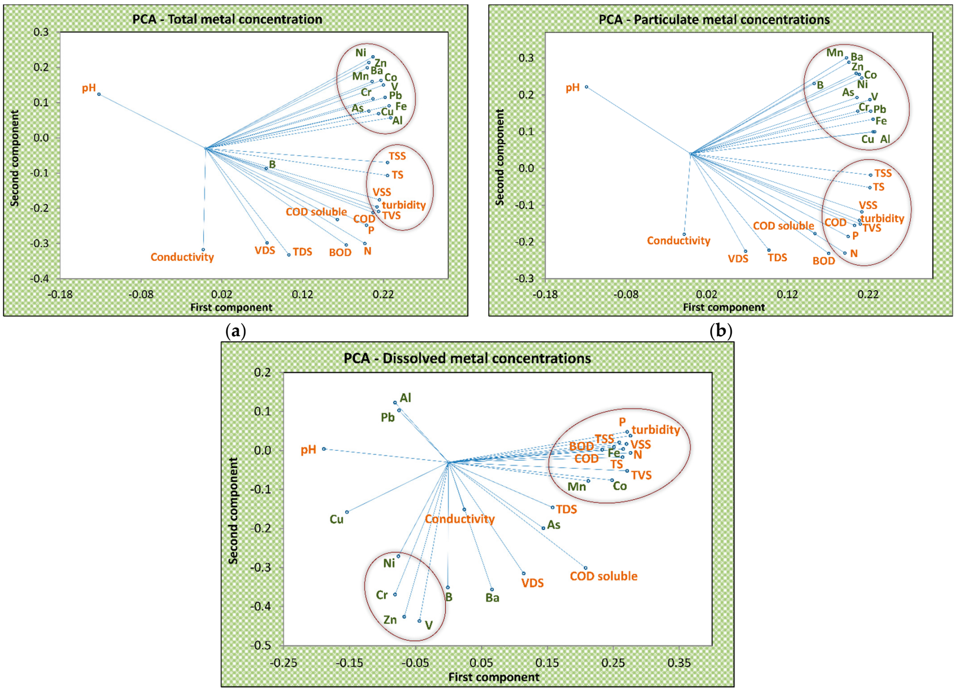
3.2. Surrogate Parameters

3.2.1. Total Hm Concentration

The results showed through a PCA the existence of four components, which explained 90.4% (total variance) of the behavior of conventional parameter and total HM concentrations in road runoff (determinant < 0.001). The first two components explained 78.3% of the behavior of the parameter concentrations considered (see phase 1 in Table 5). In the first component, the following conventional water quality parameters were associated: TS > TSS > VSS > VTSS > TUR > COD > TP > TN > BOD_5 > COD > pH. The HMs associated with the first component were as follows: Al > Fe > Pb > V > Co > Cu > Cr > Ni > Mn > As > Zn > Ba. Most of the HMs were explained by the first component (Figure 2a). The findings suggested in order of importance TS and TSS as those surrogate parameters for the indication of total HM concentrations. Kayhanian et al. [51] and Barbosa and Fernandes [53] also reported TS and TSS as surrogate parameters for the indication of total HM concentrations. The results also suggested Al and Fe as those surrogate elements for total concentrations of the other HMs under study. Except for B, which showed the lowest association coefficient in relation to the water quality parameters and HMs identified in the first component. This behavior in the total B concentration could be associated with the proximity of the study road to the sea. Montoya-Mayor et al. [54] reported a significant influence of the sea on B concentrations in continental areas. Namely, concentrations of this HM were possibly dominated by inputs from the ocean rather than from the road environment under study. Subsequently, a second PCA was performed to exclusively identify the importance of TS and TSS as surrogate parameters for total HM concentrations in road runoff. In this analysis, B was not considered. The results showed the existence of two components, which explained 93.8% of the behavior of the conventional parameter and total HM concentrations. Therefore, the results suggested that TSS were more influential earlier than TS, as a surrogate parameter for total HM concentrations in road runoff (see phase 2 in Table 5). In this PCA, it was observed that all the HMs considered were explained above 89.1%. Lastly, the findings hinted that total Fe concentrations were better explained compared to total Al concentrations.

Table 5. PCA results for concentrations of conventional parameters and HMs under scenarios of higher- and lower-energy runoff events.

	Total Concentration			**Particulate Concentration**			**Dissolved Concentration**		
Phase 1	All samples	TSS > Median	TSS < Median	All samples	TSS > Median	TSS < Median	All samples	TSS > Median	TSS < Median
Significant components	4	4	5	4	4	5	5	6	5
Variance (%)	90.4	91.2	93.5	91.5	91.6	91.5	83.8	88.2	92.4
Variance (%)—first two components	78.3	78.5	66.3	81.0	80.8	63.0	61.0	61.5	63.2
Variance (%)—first component	68.0	66.3	39.3	69.3	67.0	38.0	45.1	46.4	41.4
Preliminary parameters (Variance in %)	TS (96.6) > TSS (96.3)	TS (95.8) > TSS (95.6)	VSS (92.0) > TUR (68.2) > TSS (64.3)	TSS (96.4) > TS (96.2)	TSS (95.7) > TS (95.3)	VSS (91.2) > TUR (82.6) > TSS (69.2)	TN (96.3) > TUR (96.1) > TP (94.6) > VTS (94.5) > VSS (94.1) > COD (92.5) > TS (92.2) > TSS (90.3)	TN (95.6) > TUR (95.5) > TP (93.9) > VTS (93.8) > VSS (93.0) > COD (91.2) > TS (90.4) > TSS (88.1)	CODs (86.9) > VDS (78.1) > TS (72.9)
Preliminary HMs (variance in %)	Al (98.2) > Fe (97.2)	Al (98.0) > Fe (96.9)	Mn (96.7) > Pb (94.5) > Co (93.8) > Al (92.8) > Fe (90.0)	Al (98.8) > Fe (97.9)	Al (98.7) > Fe (97.7)	Fe (98.9) > Al (98.8)	Co (86.7) > Fe (81.4)	Co (85.7) > Fe (85.3)	Cr (92.4) > Mn (91.7) > V (89.8) > Pb (83.4) > Fe (67.4)
	Total concentration			Particulate concentration			Dissolved concentration		
Phase 2	All samples	TSS > Median	TSS < Median	All samples	TSS > Median	TSS < Median	All samples	TSS > Median	TSS < Median
Parameters identified	TS > TSS	TS > SST	VSS > TSS	TSS > TS	TSS > TS	VSS > TSS	VTS > TS	VTS > TS	VDS > TS
Significant components	2	1	3	1	1	3	4	4	4
Variance (%)	93.8	88.9	85.1	91.3	89.8	84.5	81.0	79.2	79.2
Variance (%)—first two components	93.8	-	74.6	-	-	73.9	57.9	58.7	56.3
Variance (%)—first component	90.1	88.9	61.0	91.3	89.8	60.8	35.5	38.0	32.1
Definitive parameters (Variance in %)	TSS (91.4) > TS (90.4)	TSS (89.5) > TS (88.2)	VSS (87.1) > TSS (63.9)	TSS (91.1) > TS (89.6)	TSS (89.0) > TS (87.1)	VSS (88.2) > TSS (70.6)	VTS (84.7) > TS (82.7)	VTS (80.1) > TS (77.9)	TS (75.5) > VDS (51.1)
Definitive HMs (variance in %)	Fe (99.1) > Al (98.5)	Fe (98.7) > Al (97.8)	Mn (94.5) > Co > Al (92.4) > Zn (90.8) > Fe (90.1)	V (99.4) > Fe (98.9) > Al (98.2)	V (99.5) > Fe (98.7) > Al (97.8)	Al (96.6) > Fe (95.3)	Co (92.3) > Mn (85.5) > Fe (78.3)	Co (92.0) > Mn (83.3) > Fe (81.3)	Co (91.7) > Mn (86.1) > Fe (72.3)



(**a**) (**b**)

(**c**)

Figure 2. PCA diagram for the identification of conventional water quality parameters as substitutes for the (**a**) total, (**b**) particulate, and (**c**) dissolved HM concentration in road runoff.

The findings showed that during higher-energy runoff events (median > TSS concentration), the trend was comparatively like that observed for all detected runoff events. A PCA showed the existence of four components, which explained 91.2% of the behavior of the conventional parameter and total HM concentrations (phase 1 in Table 5). In the first component, the following conventional water quality parameters were associated: TS > TSS > VSS > VTS > TUR > COD > TP > TN > COD > BOD_5. The HMs associated with the first component were as follows: Al > Fe > Pb > V > Cu > Co > Cr > Ni > Mn > Zn > Ba > As. All the HMs were explained by the first component, as in the PCA performed for all runoff events. Initially, the findings suggested that during higher-energy runoff events TS and TSS were the best surrogate parameters for the indication of total HM concentrations. The results also hinted that Al and Fe were the best surrogate HMs for the other metallic elements under study. A second PCA considering exclusively TS, TSS, and all HMs confirmed the importance of these two conventional water quality parameters (TSS > TS; phase 2 in Table 5). These are surrogate parameters of the total HM concentration during the higher-energy runoff events. On this occasion, there was a single component that explained 88.9% of the behavior of the variables considered. In this PCA, the results for more than 86.9% of the HMs were explained. The Fe and Al stood out in order of importance as the best surrogate elements in the total fraction for the other study HMs. Herngren et al. [55] reported that TSS concentration was significantly associated with rainfall intensity, and consequently, with road runoff flow. This is especially for events of high rainfall intensity. During these high energy events both coarse and fine particles accumulated in dry weather on the road surface were effectively removed (transport and dissolution) [28]. Namely, washing of road sediments and HMs associated with them was more effective during these higher energy events [56].

The results showed that during the lower-energy runoff events (TSS concentration < median), the observed trend was comparatively different from that observed for the runoff scenarios of all events and higher energy. On this occasion, more principal components were required to explain 93.5% of the behavior of conventional parameter and total HM concentrations in road runoff (5 components, phase 1 in Table 5). In the first component, the following conventional water quality parameters were associated: VSS > TUR > TSS > CON. The HMs associated with the first component were as follows: Mn > Pb > Co > Al > Fe > Zn > Cu > Ba > Ni. Thus, a comparative reduction was observed in the quantity of conventional water quality parameters (−60%) and HMs (−25%) explained by the first component. This in relation to the results obtained for the scenario of higher-energy runoff events. The results initially hinted that it was more difficult to detect surrogate parameters for the indication of total HM concentration during lower-energy runoff events, i.e., a greater number of principal components were necessary. However, in the group of possible surrogate parameters (associated with the first component), TSS, Al, and Fe were again observed. In these lower-energy runoff events, VSS stood out before TSS. Gromaire-Mertz et al. [57] reported a direct relationship between the VSS concentration and the organic matter content in the urban road runoff of roofs, gardens, and roads. These researchers also reported that TSS from road runoff had a greater association with organic fraction rather than mineral fraction (SSV/SST = 55%). However, in our study, this ratio was 36.9%. Namely, TSS was possibly more associated with mineral fraction than with organic fraction (VSS). Aryal et al. [58] reported that HMs from road runoff did not tend to be associated with VSS. Moreover, VSS (organic fraction) were associated with the finest particles accumulated in dry weather on road surfaces [59]. These fine particles (VSS) were probably the most easily transported during lower-energy runoff events [60]. This is compared to the coarser particles of road sediment (mineral fraction). All the above possibly supported the observed change in the behavior of total HM concentrations during lower-energy runoff events.

3.2.2. Particulate HM Concentration

A PCA for the particulate HM concentration showed the existence of four components, which explained 91.5% of the behavior of the conventional parameter and HM concentrations. In the first component, the following conventional water quality parameters were associated: TSS > TS > VSS > VTS > TUR > COD > TP > TN > BOD_5 > COD > pH. This trend was like that observed for the total HM concentration scenario, except that there was alternation in the order between TSS and TS. The HMs in particulate form associated with the first component were as follows: Al > Fe > Cu > Pb > V > Ni > Co > Cr > As > Zn > Ba > Mn (Figure 2b). All the HMs were explained by the first component. However, the order of importance changed slightly (e.g., Cu gained positions) in relation to the total HM concentration scenario, although Al and Fe continued to remain as the best surrogate elements for the other HMs. The findings suggested in order of importance TSS and TS as those surrogate parameters for the indication of particulate HM concentration in road runoff. However, the level of association decreased slightly (TSS = −0.21%; TS = −0.41%) in relation to that observed for the total HM concentration scenario. Thus, the results suggested that regardless of the fraction considered (total or particulate), TS and TSS were highlighted as those surrogate parameters for HM concentration in road runoff (phase 1 in Table 5). A second PCA was performed considering TSS and TS exclusively. The results showed the existence of a single component, which explained 91.3% of the behavior of the conventional parameter and particulate HM concentrations in road runoff. On this occasion, TSS were more influential than TS as surrogate parameters for the indication of particulate HM concentration (phase 2 in Table 5). More than 92.6% of the results of all the HMs considered were explained. Moreover, 98.9% and 98.2% of the results for the concentrations of Fe and Al were explained, respectively. These HMs were in the group of parameters that showed the best association with the other metallic elements, except that on this occasion, they were preceded by V.

The results showed that during higher-energy runoff events the trend in particulate concentration was comparatively like that observed for the total HM concentration scenario. Namely, a PCA evidenced the existence of four components, which explained 91.6% of the behavior of the conventional parameter and particulate HM concentrations in road runoff. In the first component, the following conventional water quality parameters were associated: TSS > TS > VSS > VTS > TUR > COD > TP > TN > BOD_5 > COD. The HMs associated with the first component were as follows: Al > Fe > Cu > Pb > V > Ni > Cr > Co > Zn > As > Ba > Mn. The findings suggested that during higher-energy runoff events, TSS and TS were the best surrogate parameters for the indication of particulate HM concentration (phase 1 in Table 5). The results also hinted that Al and Fe were the best surrogate HMs for the indication of the other metallic elements under study. A second PCA considering exclusively TSS, TS and all HMs again confirmed the importance of these two conventional water quality parameters (phase 2 in Table 5). This are surrogate parameters for the indication of the particulate HM concentration during higher-energy runoff events. On this occasion, there was a single component that explained 89.8% of the behavior of the variables considered. In this analysis, more than 91.6% of the results of all HMs were explained. Fe and Al stood out in order of importance as the best surrogate parameters for the other HMs in the particulate fraction. However, V also stood out under this particulate concentration scenario in higher-energy events.

The results showed that during lower-energy runoff events, the observed trend was comparatively different. Thus, five main components were required to explain 91.5% of the behavior of the conventional parameter and particulate HM concentrations in road runoff. The first two components only explained 63.0% of the concentrations observed for all the parameters considered (phase 1 in Table 5). In the first component, the following conventional water quality parameters were associated: VSS > TUR > TSS > CON. The HMs associated with the first component were as follows: Fe > Al > Co > Ni > Mn > Zn > Pb > Cu > As. A reduction was observed in the quantity of water quality parameters (−60%) and HMs (−25%) explained by the first component. This is relative to the results obtained for higher-energy runoff events. The results hinted that it was more difficult to detect conventional water quality parameters surrogate for particulate HM concentration during lower-energy runoff events, i.e., a greater number of principal components were needed. However, in the group of possible surrogate parameters, TSS, Fe, and Al were again observed (phase 2 in Table 5). VSS was highlighted over TSS in these lower-energy runoff events.

3.2.3. Dissolved HM Concentration

The results showed through a PCA for the dissolved HM concentration the existence of five components, which explained 83.8% of the behavior of the conventional parameter and HM concentrations. In the first component, the following conventional water quality parameters were associated: TN > TUR > TP > VTS > VSS > COD > TS > TSS > BOD_5 > COD > pH > DTS. This order of importance was different from that observed for the scenarios of total and particulate HM concentration in road runoff. The HMs in dissolved form associated with the first component were as follows: Co > Fe > Mn > Cu (Figure 2c). On this occasion, not all the results for the HMs were explained by the first component. However, Fe remained in the group of possible surrogate HMs. TS and TSS also remained within the group of possible surrogate parameters for the dissolved HM concentration (phase 1 in Table 5). A second PCA was carried out considering exclusively VTS and TS. The results showed the existence of four components, which explained 81.0% of the behavior of the conventional parameter and dissolved HM concentrations in road runoff. Indeed, VTS was more influential compared to TS as surrogate parameter for the indication of dissolved HM concentrations (phase 2 in Table 5). Lastly, dissolved Fe concentration was explained by 78.3%. However, under this scenario, Co (92.3%) and Mn (85.5%) showed better behavior as possible surrogate elements for the other HMs under study.

The results showed that during higher-energy runoff events the trend in the dissolved fraction was different from that observed for the total and particulate HM concentration scenarios in higher-energy events. Namely, a PCA evidenced the existence of six components, which explained 88.2% of the behavior of the conventional parameter and dissolved HM concentrations. In the first component, the following conventional water quality parameters were associated: TN > TUR > TP > VTS > VSS > COD > TS > TSS > BOD_5 > COD > pH. The HMs associated with the first component were as follows: Co > Fe > Mn > As. TS and TSS remained within the group of possible surrogate parameters for the dissolved HM concentration in road runoff. Fe also remained within the group of possible surrogate HMs (phase 1 in Table 5). A second PCA was carried out considering exclusively VTS and TS. The results showed the existence of four components, which explained 79.2% of the behavior of the conventional parameter and dissolved HM concentrations in road runoff. On this occasion, TS was explained by 77.9%. Lastly, dissolved Fe concentration was explained by 81.3%. However, under this scenario, Co (92.0%) and Mn (83.3%) showed better behavior as possible surrogate elements for the other HMs under study.

The results showed that during lower-energy runoff events the trend observed in the dissolved fraction was possibly the most different in relation to all the scenarios considered in this study. Five principal components were required to explain 92.4% of the behavior of conventional parameter and dissolved HM concentrations in road runoff. In the first component, the following conventional water quality parameters were associated: pH > COD > VDS > TS > COD > TP > VTS > CON. The HMs associated with the first component were as follows: Cr > Mn > V > Pb > Fe > As > Al. Thus, a reduction in the quantity of water quality parameters (−37.5%) and an increase in HMs (75%) explained by the first component were observed. This is in relation to the results obtained in the dissolved fraction for the higher-energy runoff events. The results hinted that it was more difficult to detect surrogate conventional parameters for the indication of the dissolved HM concentration during lower-energy runoff events, i.e., a greater number of principal components were necessary. Lastly, in the group of possible surrogate parameters, TS and Fe were again observed. In these events of lower-energy runoff in the dissolved fraction, VDS and TS were highlighted.

3.3. Road Runoff Energy Scenarios

Based on the findings observed for HM concentrations (total, particulate, and dissolved), we proceeded to analyze the energy scenarios for the runoff events considered: (1) all events, (2) higher-energy events, and (3) lower-energy events. Overall, the results suggested that regardless of the runoff event energy, the best conventional parameter surrogate for total HM concentrations was TSS. Moreover, the best HM surrogate for the other metallic elements was Fe. Indeed, these findings are like those reported by other studies (e.g., [51,53]). However, when the runoff event energy decreased, the results suggested VSS rather than TSS as a surrogate parameter for total HM concentrations (phase 2 in Table 5). Under this scenario, Co and Mn stood out as the best surrogate metallic elements compared to Fe. In other words, the higher- and lower-energy runoff events possibly had a differentiated behavior in relation to the identification of surrogate parameters for the indication of total HM concentrations.

In general terms, the results showed that the particulate fraction in road runoff had a behavior like that observed for the total fraction (phase 2 in Table 5). That is, it was evidenced that TSS and Fe were the best surrogate parameters, and that there was possibly a differentiated behavior between the higher- and lower-energy runoff events. This similar behavior between the total and particulate fraction suggested that the behavior of HM concentrations in road runoff was mainly explained by the particulate fraction rather than by the dissolved fraction. Thus, we proceeded to analyze the percentage of HMs associated with the particulate fraction during the higher- and lower-energy runoff events. The results suggested that during the higher energy events the surrogate HMs in the total fraction were Fe and Al, and that during the lower energy events, the surrogate HMs were Mn and Co (phase 2 in Table 5). In this study, these HMs were associated with the particulate fraction in a percentage greater than 70% during the higher- and lower-energy runoff events (Figure 3). Indeed, Fe was the metallic element with the highest percentages of association with the particulate fraction during runoff events (98–99%). Therefore, the results suggested that HMs with high percentages of association with the particulate fraction of road runoff were the best surrogates for the other HMs under study. Certainly, the particulate fraction was the one that possibly explained the behavior of HM concentrations in road runoff. For the identified surrogate HMs (Fe, Al, Mn, and Co), the findings showed that during the higher- and lower-energy runoff events the percentages of association with the particulate fraction were between 84–99% and 77–98%, respectively. On average, for all HMs, higher-energy runoff events associated 18.5% more metallic elements in the particulate fraction compared to lower-energy runoff events. Hence, the particulate fraction was fundamental to explain the behavior of the HM concentrations in road runoff.

The findings showed that TSS and VSS were associated with higher- and lower-energy runoff events, respectively, for the total and particulate HM fractions. In relation to the dissolved fraction, the results showed that there was probably a greater affinity with the volatile fraction of the solids transported by road runoff (phase 2 in Table 5). Namely, the dissolved fraction had a greater importance during lower-energy runoff events. Memon and Butler [59] reported that the volatile fraction tended to associate with the finer particles carried by road runoff. Thus, the findings hinted that the behavior of HM concentrations in road runoff during higher- and lower-energy runoff events was explained by the particle size associated with the HM emission source. During the higher-energy runoff events, both coarse particles (particulate fraction) and fine particles from the road sediment (dissolved fraction) were possibly transported. In contrast, during lower-energy runoff events, only the finest particles (dissolved fraction) of the road sediment were possibly transported. Other studies also reported the importance of particle size associated with each HM in explaining its washing during road runoff events (e.g., [23,28]). As mentioned, the HM concentrations in road runoff were better explained by the particulate fraction rather than by the dissolved fraction. In this study, the relationship between VSS/TSS was 0.369. Therefore, the previous findings supported the TSS identification as the surrogate parameter for total and particulate HM concentrations in road runoff for higher-energy runoff events.

During lower-energy runoff events, the results suggested VSS as the surrogate parameter for total and particulate HM concentrations.

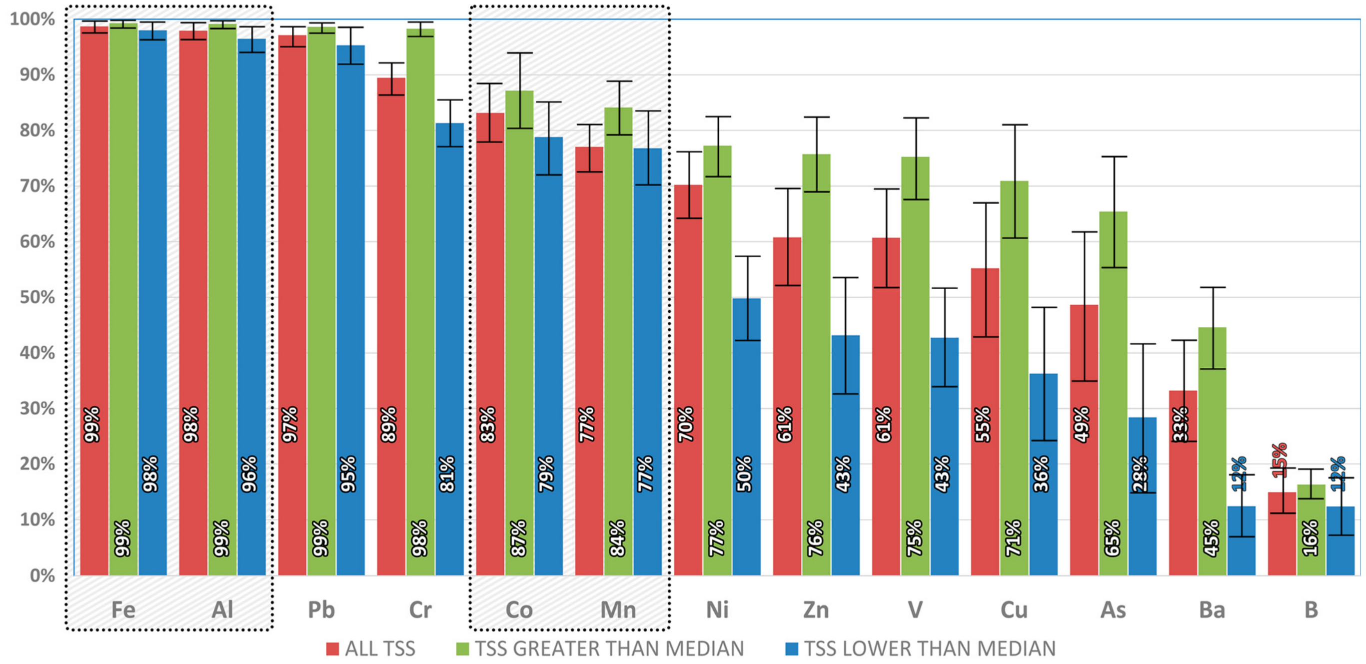


Figure 3. Percentage of HMs associated with particulate fraction during higher (green) and lower energy (blue) runoff events. In the boxes, the surrogate HMs identified during the higher (green) and lower energy (blue) runoff events.

In relation to surrogate HMs, the results suggested Fe as the best metallic element during the higher-energy runoff events (total and particulate fraction). Moreover, this trend suggested that Fe was more associated with the particulate fraction (larger particles) rather than the dissolved fraction (smaller particles). For lower-energy runoff events, the results suggested Co and Mn as those surrogate HMs (dissolved fraction). This trend suggested that Co and Mn had a greater preference for the dissolved fraction compared to Fe. However, Fe, Co, and Mn were always associated with particulate fraction above 70% during higher- and lower-energy runoff events (Figure 3). Figure 4 shows the adjustment statistics for the linear regression models developed between the concentrations of all the parameters identified as surrogates for all runoff events.

Finally, the main limitations detected during the development of this study were the following: (i) The results obtained were conditioned by the characteristics (climatic, morphological, and anthropic) of the study site. That is, the influence of these characteristics did not make it possible to generalize the findings of this study to other urban road basins. (ii) A greater number of rainfall events would have been desired. In effect, this would have increased the sample size considered in this study.

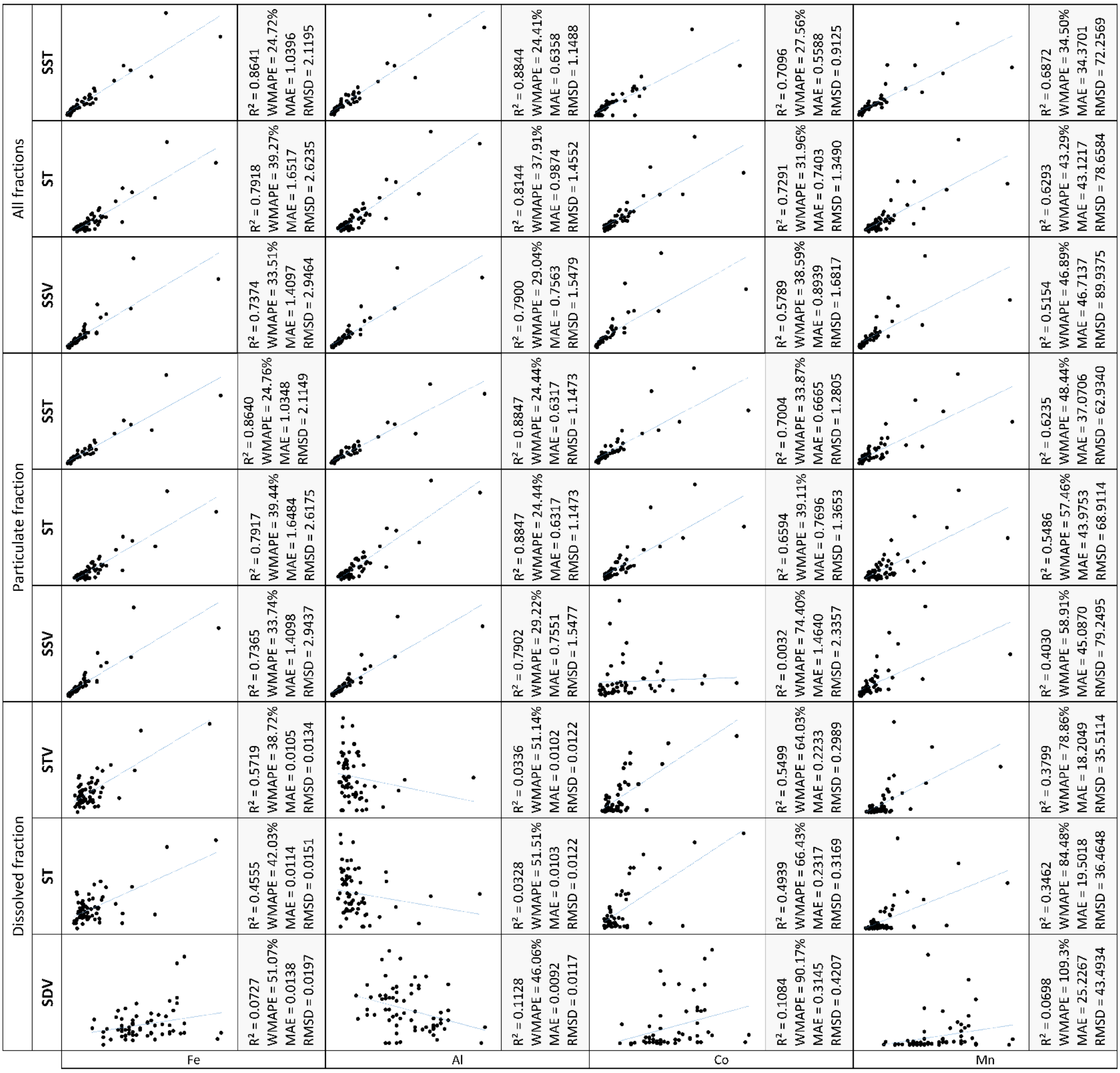


Figure 4. Adjustment statistics of the regression models developed for the surrogate parameters identified in the road runoff. R^2 = Determination coefficient, WMAPE = Weighted mean absolute percentage error, MAE = Mean absolute percentage error, and RMSD = Root mean square deviation.

4. Conclusions

The results of this study on the identification of possible surrogate conventional physicochemical parameters of pollution by HMs in urban road runoff allow us to visualize the following conclusions.

1. The results suggested that it was easier to detect surrogate parameters for total HM concentrations during higher-energy runoff events. During the lower-energy runoff events, a greater number of principal components (PCA) were observed due to lower percentages of association between the variables considered (conventional parameters and HMs).
2. In this study, it was observed that the total HM concentration in road runoff was better explained by the particulate fraction rather than by the dissolved fraction. Higher-

energy runoff events were associated with the particulate fraction and lower-energy runoff events were associated with the dissolved fraction.

3. The results hinted that regardless of the runoff event energy, it was easier to detect conventional surrogate parameters for the particulate HM concentration compared to the dissolved HM concentration.
4. The results suggested that during the higher-energy runoff events, a more comprehensive view of the study phenomenon was obtained, which allowed a better analysis of the behavior of the total HM concentrations in road runoff. In other words, during the higher-energy runoff events, both coarse particles (particulate HM fraction) and fine particles from the road sediment (dissolved HM fraction) were possibly transported. In contrast, during lower-energy runoff events, only the finest particles (dissolved HM fraction) of the road sediment were possibly transported.
5. The findings indicated for total HM concentration that the best surrogate parameter during higher-energy runoff events was TSS. The best surrogate HM during these runoff events was Fe. The results also suggested that HMs with high percentages of association with the particulate fraction (>70%) of road runoff were the best surrogates for the other HMs under study. For lower-energy runoff events, the best surrogate parameter was VSS, although TSS also showed good behavior.
6. The dissolved HM concentration tended to be associated with the volatile fractions of solids present in road runoff (e.g., VTS and VDS). Co and Mn were better surrogates for this fraction compared to Fe. However, Fe also showed high percentages of association in relation to the other metallic elements under study.

Finally, this study is relevant for the institutions responsible for monitoring and controlling the runoff water quality because it allows to visualize additional methods to forecast the total HM concentrations from conventional parameters, which can reduce the costs associated with their monitoring. Moreover, this study allows us to deepen the knowledge in relation to the design of road runoff treatment systems. That is, the designers of these treatment systems have additional criteria to consider based on the findings of this study. The following future lines of research are visualized. 1) Carry out additional studies on urban roads with other climate (rainfall intensity), morphological (road slope and pavement type), and anthropic (traffic intensity and land use) characteristics. 2) Develop research in laboratory models to have greater control over the climate, morphological, and anthropic variables of interest.

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