A simplified method for determining potential heavy metal loads washed-off by stormwater runoff from road-deposited sediments

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Abstract: A simplified method is proposed for determining the potential load of heavy metals (HMs) derived from the wash-off caused by surface runoff on road-deposited sediment (RDS). The method consists of three phases: (i) characterization of RDS load wash-off, (ii) assessment of HM load in dry weather, and (iii) application of a wash-off equation. Two processes were included in the wash-off equation: HM transport (solid fraction) and HM leaching (dissolved fraction). The average wash-off of HMs ranges from 16.6 to 46.3%, relative to the total mass of HMs associated with dry-weather RDS (Pb, Zn, Cu, Cr, Ni, Cd, Fe, Mn, Co, and Ba). Cd, Mn, and Zn presented the highest wash-off in the areas studied. The size fraction below 250 µm contributed an average of 86.7% of potential HM load washed-off from RDS. Based on the phenomena included in the wash-off equation, it was observed the following order of precedence: transport of RDS < 250 µm, leaching of RDS < 250 µm, and leaching of RDS ≥ 250 µm. Solid and dissolved fractions contributed 70.7 and 29.3% of the potential HM load washed-off by runoff from RDS, respectively. The proposed method serves as a management tool for road HM pollution during rain.

Keywords: Heavy metal; Road-deposited sediment; Road runoff; Wash-off; Water quality.

1. Introduction

Diffuse contamination generated by surface runoff is a key factor in the deterioration of water-body quality in urban areas (Helmreich et al., 2010; Martínez and Poleto, 2014; Wijesiri et al., 2016). The importance of and interest in determining such loads stems from many studies that have reported the high presence of heavy metal (HM) concentrations in dissolved form in urban water bodies (e.g., Stagge et al., 2012; Kumar et al., 2013a; Maniquiz and Kim, 2014). Moreover, studies have analyzed HMs associated with the solid fraction of surface runoff, namely the portion of road-deposited sediment (RDS) accumulated in dry weather that is washed-off during rainfall events (Bian and Zhu, 2009; Aksoy et al., 2012). Thus, RDS are carriers for potentially toxic pollutants such as HMs (Egodawatta et al., 2013), transforming them into an important environmental medium for assessing contaminant levels in urban systems (Sutherland, 2000).

Extensive research has been done on the effects of wash-off caused by surface runoff with respect to the RDS-related HMs (e.g., Davis and Birch, 2010; Zhao and Li, 2013). Most of this research has relied on total HM concentrations (solid and dissolved fraction sums) in runoff as the prime indicator of wash-off for developing equations and models of these surfaces. Thus, diffuse-contamination models have been used in urban areas to estimate the pollutant loads associated with runoff, such as SWMM, STORM, SLAMM, HSPF, DR3M-QUAL, MOUSE, MUSIC, and P8-UCM (Shaw et al., 2006; Elliott and Trowsdale, 2007; Zhao et al., 2014). However, these models entail significant preparation in terms of parameterization and calibration data; for example, data are required for rainfall intensity, antecedent dry period (ADP), pollutant buildup, and wash-off rates as well as drainage-basin morphology. Yet, scant research has been conducted on the wash-off phenomenon of runoff-caused HMs using dry-weather RDS as an indicator (e.g., Herngren et al., 2006; Kayhanian et al., 2012; Zhao and Li, 2013). Most research efforts have focused on the direct study of HM concentrations linked to road runoff before evaluating the wash-off phenomenon using RDS between rainfall events (i.e., in dry weather). Approaches that include dry-weather RDS have sought to simplify existing models of wash-off caused by stormwater runoff. Probably the main benefit of this latter approach is that only required information from the mass amount (load) of HMs associated with the RDS before and after each rainfall event to determine the HM load washed-off by stormwater runoff.

Two mechanisms influence RDS wash-off during rainfall events. The first is related to the material in particle form, which detaches as a result of the direct impact of rainfall (Huber, 1992). The second is related to the soluble fraction, which dissolves, and due to remove subsequent, becomes turbulent, favoring RDS transport and mixture/leaching (Collins and Ridgway, 1980). Wash-off rates for RDS during rainfall events depend on event intensity, physical characteristics of road surfaces (e.g., road slope, influence of curbs and street sweeping), and particle size distribution (Sartor et al., 1974). Studies on the wash-off phenomenon of HMs caused by road runoff have shown that rainfall intensity and ADP are the leading climate factors (e.g., Bian and Zhu, 2009; Zafra et al., 2011; Stagge et al., 2012; Egodawatta et al., 2013). RDS transport caused by road runoff (wash-off) increases with rainfall intensity (Lee et al., 2004; Zhao et al., 2010; Zhao and Li, 2013) and longer ADPs (Helmreich et al., 2010). Malmquist (1978) and Reinertsen (1981) reported that intense (> 10 mm/h) and successive (four events on consecutive days) rainfall events decreased RDS load by nearly 80%. Ball et al. (1998) found evidence that only rainfall events with intensities greater than 7 mm/h should be considered transport events for RDS-related HM loads.

In addition to causing RDS transport, runoff leads to leaching, which must be considered when analyzing the wash-off phenomenon. Ellis and Revitt (1982) studied the effects of leaching on RDS and reported the following sequence (based on leaching test for rainwater, mechanical shaker, pH = 6.5, *t* = 28 days): Cd > Zn - Cu > Pb. These researchers reported that the leaching test allowed the simulation of turbulent runoff conditions on RDS during storm drainage from the roadside surface. Stone and Marsalek (1996) obtained a similar sequence for leaching tests on RDS with the sequential-extraction procedure reported by Tessier et al. (1979), with exchangeable cations phase, $MgCl_2$, 1M, pH = 7, *t* = 1 hour: Cd - Cu > Zn > Pb. Recent studies have indicated a similar sequence using the Community Bureau of Reference of the European Commission’s (BCR) three-stage sequential extraction procedure (acid extractable phase: CH_3-COOH, 0.11M, *t* = 16 hours): Zn - Cu > Pb (Kumar et al., 2013a; Li et al., 2015). These findings have led researchers to suggest that RDS acts as an effective sink for Pb but not Cd or Cu. However, dissolved organic matter and pH are the most important solution parameters affecting the mobility of metals from RDS (Rijkenberg and Depree, 2010).

Together, the previous studies on HM leaching allow us to suggest that the acid-extractable phase (water soluble, exchangeable, and bound to carbonate) is ideal for simulating turbulent runoff conditions during storm drainage from the roadside surface. HM content for this phase has been considered to provide a reasonable approximation of the bioavailable HM content in RDS (Stone and Marsalek, 1996). However, sequential extractions rely on chemical reagents different from those found in the digestive tract of deposit-feeder organisms in aquatic systems, where there is an abundance of hydrolytic enzymes and chemicals derived from predigestion (Mayer et al., 1997). Consequently, some researchers have questioned the use of these chemical reagents for quantifying the bioavailable fraction (Turner and Olsen, 2000; Rosado et al., 2016). Also, in the available literature there were limited discussions on relationship between the sorption behavior of HM species and the water quality of road runoff (e.g., dissolved organic carbon content and pH). Therefore, in the present study, turbulent runoff conditions were simulated mainly using the DIN 38414-S4 standard (DIN, 1984): deionized water, mechanical shaker, 10 rpm, room temperature, and t = 24 hours.

No consensus has been reached with regard to the determination of the sediment-load buildup and wash-off on the road surfaces (e.g., Sartor et al., 1974; Vaze and Chiew, 2002; German and Svensson, 2002; Egodawatta et al., 2013). This lack of consensus is primarily attributable to variable study-site conditions and the effectiveness of the method used for RDS collection (e.g., dry vacuuming, dry sweeping, dry vacuuming and sweeping, and simultaneous washing and vacuuming). Perhaps the most comprehensive summary of surface accumulation and pollutant-fraction data is provided by Manning et al. (1977). These authors also discussed the many problems and facets of sampling and measurements. Suffice it to say that particle size characteristics and degree of removal from the road surface differ for each sampling method. In this study, RDS was collected via dry vacuuming and sweeping because the proposed method was based on the characterization of dry-weather RDS.

In the analysis of HM content in RDS, the fine-size fraction was given particular attention because the consulted literature suggested that this fraction tends to present the highest HM concentrations. On average, the size fraction below 250 μm accumulated 69% (between 51.2 and 82.5%) of total HM load (Mn, Cd, Zn, Cu, Pb, Co, Ni, Fe, and Cr) associated with RDS in dry weather (Sartor et al., 1974; Ellis and Revitt, 1982; German and Svensson, 2002; Zanders, 2005; Bian and Zhu, 2009; Zhao et al., 2010; Kayhanian et al., 2012; Ma and Singhirunnusorn, 2012; Bi et al., 2013). Per these authors, the fine-size fraction of RDS (e.g., < 250 μm) served as a representative fraction for the characterization of dry-weather HM content.

In light of this background, the objective of this paper was to present the development of a simplified method for determining the potential HM loads derived from wash-off caused by stormwater runoff on RDS. Potential HM load was determined relative to the total mass of RDS-associated HM in dry weather. The method consisted of three phases: (i) characterization of RDS load wash-off, (ii) assessment of HM load in dry weather, and (iii) application of a wash-off equation. Two processes were included in the wash-off equation:

HM transport (solid fraction) and HM leaching (dissolved fraction). The focus in this paper was on the following HMs: Pb, Zn, Cu, Cr, Ni, Cd, Fe, Mn, Co, and Ba. These HMs were the most reported by studies on RDS (e.g., Ellis and Revitt, 1982; Stone and Marsalek, 1996; Bi et al., 2013; Zannoni et al., 2016).

2. Materials and Methods

2.1. Study areas

The road surfaces for developing the simplified method were located in the cities of Torrelavega, Spain (A1) and Soacha, Colombia (A2). Each road surface had two sections: A11 and A12, and A21 and A22, respectively. These study areas were selected because the climate conditions, road-traffic density, and land use were different for each road surface. Table 1 shows the primary climate and physical characteristics for each road. Climate data (daily) were obtained from stations located between 40 and 4250 m from the road-surface curbs studied. In A1, the Atlantic climate (warm) is characterized by abundant yearlong rains, high humidity, and mild temperatures. In A2, the tropical mountain climate (cold) is characterized by abundant yearlong rains and a wide variation in temperature (hourly variation: 5-22 °C).

2.2. Sampling

The protocol for RDS collection followed the sampling systems developed by previous authors (Ellis and Revitt, 1982; Vaze and Chiew, 2002; Bian and Zhu, 2009). RDS samples were collected next to the curb (within 0.50 m) in dry weather at the same time each day for a period of 65 and 127 days for A1 (09/28/2004-12/01/2004) and A2 (01/07/2010-05/14/2010), respectively. The sampling surface's area was 0.50 m^2 (707 mm x 707 mm). The weight of each RDS was between 10 and 180 g per square meter. Collection-area sizes were ensured via the surface placement of an acrylic frame. For RDS collection, a vacuum cleaner (1.5 kW) capable of retaining particles larger than 1 μm was used in tandem with a plastic-fiber brush. The RDS collection system had two stages. The first stage consisted of direct vacuuming of the sediment from the road surface (done three times). The second stage consisted of sweeping the same surface with a plastic-fiber brush, so the sediments stuck to the surface could be vacuumed (done three times). This dual-step sampling sequence (vacuuming and sweeping-vacuuming) helped avoid suspension-related loss of the fine-size fraction of the RDS, which an initial sweep of the surface with the brush may have caused. The sampling surface was lightly swept to prevent loosening of the pavement particles, and an attempt was made to apply the same force when brushing throughout the sampling period. The total amount of sediment on the road surface was calculated as the sum of the RDS collected in the two stages. The sampling site was controlled to prevent repetition and ensure proximity to previous collection points. On average, the RDS samples were taken daily for A1 and every three days for A2. Slight variations in sampling frequency were caused by rainfall events, which prevented dry-weather RDS. Fifty-six and 88 RDS samples were collected in A1 (A11 and A12) and A2 (A21 and A22), respectively (n = 144 RDS samples).

A field test on a road surface was used (done 10 times) to assess the effectiveness of the RDS collection system in dry weather. The test entailed the consecutive application of the sampling system three times to evaluate the remaining RDS load (weight) after each application (characteristics of the selected road surface: asphalt/rough; slope: 1%; collected RDS load: between 40 and 55 g). On average, the analysis showed that the effectiveness of the RDS recollection system after the first application (vacuuming and sweeping-vacuuming) was 95.5 ± 1.7, 97.2 ± 1.2, 98.1 ± 0.5, 99.2 ± 0.2, 99.6 ± 0.09, 99.9 ± 0.01, and 100% (average effectiveness: 98.4%) for size fractions of < 63, 63-125, 125-250, 250-500, 500-1000, 1000-2000, and 2000-2800 μm, respectively. The second application of the RDS collection system (on the same sampling surface) increased the average effectiveness to 99.3%, with respect to the third application. The road surfaces studied were not subjected to mechanical sweep. Therefore, we did not have to consider road sweeping a cleaning mechanism (RDS removal) during the sampling period, which meant only rainfall served as a cleaning mechanism.

2.3. Laboratory analysis

2.3.1. Particle size distribution in RDS

The particle size distribution (PSD) of RDS was determined following the ISO-11277 method (ISO, 2000). The sizes of the mesh opening used for PSD analysis were between 63 and 2800 μm (< 63, 63-125, 125-250, 250-500, 500-1000, 1000-2000, and 2000-2800 μm). A statistical analysis with the Kolmogorov-Smirnov test was performed to evaluate the normality of the PSD data set. The data were previously subjected to a logarithmic transformation to evaluate the adjustment to this probability distribution. A linear regression analysis was performed to develop a model between the particle size (μm) and mass percentage of RDS associated with each size fraction. This analysis was conducted to determine the RDS particle sizes associated with the 10 (d_{10}), 50 (d_{50}), and 90 (d_{90}) percentiles. The percentile variation was also analyzed before and after each rainfall event (n = 19 rainfall events).

Analysis of RDS susceptibility to runoff-caused wash-off accounted for particle diameter for all rainfall events at sites A1 and A2 during the sampling period. PSD before and after each rainfall event was used to assess the RDS load wash-off (difference of RDS mass before and after each rainfall event) for all size fractions. This analysis also included rainfall intensity, ADP, and road slope. A Pearson correlation coefficient analysis was performed to evaluate the relationship between the previous three variables and the RDS load wash-off after each rainfall event.

2.3.2. Leaching test

We performed a leaching test of HMs associated with RDS in line with the DIN 38414-S4 standard (DIN, 1984). This allowed for the simulation of turbulent runoff conditions during storm drainage from the roadside surface. Deionized water and RDS were mixed at an L/S ratio of 10 L/kg (100 g of RDS) dry material and mechanically shaken (Heidolph, REAX 20/4) for 24 hours at a speed of 10 rpm at room temperature in the dark. RDS leachates were obtained via filtration of the supernatant with a PTFE membrane filter (Millipore, XX1004700, pore size: 0.45 µm). Forty-eight leaching analyses were performed for A1 and A2 (24 for each study area). As noted, the leaching test simulated potential conditions of turbulent runoff on RDS; principally due to the wash-off time simulated (t = 24 hours), where in a typical storm this may be from minutes to hours. It is unlikely that all HMs leached in the laboratory (potential conditions) would leach with the same intensity during rainfall events (real conditions). However, the objective of this study was to determine the potential HM loads washed-off by rainwater runoff from RDS.

2.3.3. Digestion method

RDS samples were digested in a mixture of hydrochloric acid and nitric acid (molar ratio of 3:1, aqua regia) per the ISO-11466 method (ISO, 2000). This type of digestion was performed in 250-mL glass beakers covered with watch glasses. A thoroughly mixed RDS sample of 3.00 g was digested in 28 mL of aqua regia on a hot plate for 3 hours at 110 °C. After evaporation to near dryness, the RDS sample was diluted with 20 mL of 2% (*V/V* with H_2O) nitric acid and transferred to a 100-mL volumetric flask after filtering through Whatman no. 42 paper and diluted to 100 mL with distilled water.

2.3.4. HM content in RDS

RDS-associated HM concentration was determined via flame atomic absorption spectrometry as detailed in the ISO-11047 method (ISO, 2000). A Perkin Elmer AAnalyst 300 flame atomic absorption spectrometer was equipped with appropriate hollow cathode lamps and a 10-cm air-acetylene flame because the atomizer was used as the detector throughout the entire spectrometry process. The wavelengths for monitoring Zn, Pb, Cu, Cr, Ni, Mn, Cd, Fe, Co, and Ba were 213.9, 283.3, 324.8, 357.9, 232.0, 279.5, 228.8, 248.3, 240.7, and 553.6 nm, respectively. All instrumental settings used followed the recommendations in the manufacturer's manual.

Suitable chemical standards were used during analysis. All chemicals were of analytical reagent grade, unless otherwise indicated. Double-deionized water was used for preparing all solutions and dilutions. All stock solutions of the HMs (1000 mg/L) were prepared using the nitrate salts of HMs or corresponding pure HMs (Merck, Darmstadt, Germany). Stock solutions were diluted to produce working solutions of HMs. All glassware and plastic vessels were treated by acid water (a 1% *V/V* solution of HNO_3) for 24 hours and then rinsed with distilled water before use. HM loads for size fractions were determined through HM concentration and quantity of RDS by weight associated with each size fraction (n = 144 RDS samples by 7 size fractions).

The concentration levels were within the acceptable detection limits (LOD): Zn 0.044, Pb 0.081, Cu 0.004, Cr 0.007, Ni 0.002, Mn 0.009, Cd 0.004, Fe 0.007, Co 0.004, and Ba 0.093 mg/L. Detection limits were calculated based on the standard definition of the concentration of the analyte yielding a net signal equivalent to three times the standard deviation of the background signal: $3s/b$, $n = 24$, where s is the standard deviation of the blank and b is the slope of the calibration graph. Given that it is difficult to obtain a blank soil, the signal obtained using the reagents for each extraction stage was treated as the blank. Correlation coefficients (r) of the calibration curves were greater than 0.996 for all HMs studied. Finally, a standard reference material (SRM 2711 Montana soil from NIST) was used for quality control of the HM analysis. The recoveries varied, though all fell within 86.9 and 109%. The precision was nearly 90%, with a confidence level of 95%.

3. Results and Discussion

3.1. The simplified method

3.1.1. Characterization of RDS load wash-off

RDS particle sizes exhibited a positively skewed Log-normal distribution (7 size fractions between 63 and 2800 μm). Ellis and Revitt (1982), Ball et al. (1998), and Kayhanian et al. (2012) found similar PSD. Table 2 shows the d_{10}, d_{50}, and d_{90} (with the subscript referring to percentile) for the RDS collected from A1 (A11, A12) and A2 (A21, A22) road surfaces. The PSD of the RDS after rainfall events was coarser. On average, d_{50} was 263 to 282 μm before rainfall events and between 292 to 337 μm after rainfall events. Based on d_{50}, we proposed the size fraction below 250 μm as the dominant one in terms of RDS mass for the present study. To reiterate, the size fractions of RDS analyzed were: < 63, 63-125, 125-250, 250-500, 500-1000, 1000-2000, and 2000-2800 μm.

Table 3 shows the results obtained by RDS size fraction for analysis of susceptibility to wash-off caused by road runoff (percentage difference relative to the RDS mass before and after each rainfall event). For the size fraction below 250 μm, the analysis showed that the average percentage of RDS transported by runoff during all rainfall events in A1 (asphalt concrete, slope = 0.2-4%, intensity = 0.8-3.7 mm/h, Atlantic climate) and A2 (asphalt concrete, slope = 1-2%, intensity = 0.8-4.5 mm/h, tropical mountain climate) was 26.5 and 47.0%, respectively. Zhao and Li (2013) reported an average wash-off of RDS caused by runoff between 15.8 and 11.6% for the size fraction below 1000 µm using a rainfall simulator (asphalt concrete, slope = 4.1%, intensity = 46.7 mm/h, humid continental climate). Tian et al. (2009) found an average wash-off caused by runoff of 37.9% for the size fraction below 300 µm (humid continental climate). Vaze and Chiew (2002) reported that wash-off caused by runoff reached 45% of RDS accumulated in dry weather (asphalt concrete, slope = 10%, intensity = 4 mm in single burst, size fraction < 3000 µm, oceanic climate). The variations in the findings of previous studies can likely be attributed to variations in rainfall intensity, duration of the ADP, assessed size fraction, pavement roughness, road slope, sampling method, and accumulated RDS on road surfaces tested.

In our study, there was no significant correlation (Pearson's *r, p*-value > 0.05) between the percentage of RDS transported by runoff (wash-off), and rainfall intensity, ADP, and road slope. However, a direct relationship between these variables was observed in the information reported in Tables 2 and 3. That is, Table 3 displays an increase in the wash-off of RDS below 250 µm with increased rainfall intensity, ADP, and road slope.

3.1.2. Assessment of HM load in dry weather

Table 4 shows the distribution by size fraction of the average HM load (mg of HM per kg of RDS) associated with RDS in dry weather. For A1 and A2, an average of 62.6 and 58.0%, respectively, of the total HM load in RDS was associated with the size fraction below 250 µm. Sartor et al. (1974), Ellis and Revitt (1982), German and Svensson, (2002), Zanders (2005), Bian and Zhu (2009), Zhao et al. (2010), Kayhanian et al. (2012), Ma and Singhirunnusorn (2012), and Bi et al. (2013) reported results between 51.2 and 82.5%, with an average of 69%. These results indicate that the size fraction below 250 µm was representative of RDS and, as a result, could be used to characterize HM content in dry weather.

The order of precedence in the average HM load associated with the size fraction below 250 µm at study site A1 was: Zn > Cd - Co > Mn > Pb - Ni > Cu > Cr > Fe. At A2, the order of precedence was: Zn - Ba > Cd > Cu > Mn > Pb > Fe. On average, the HMs most associated (higher load) with the size fraction below 250 µm were Co (70%), Zn (68.5%), Cd (65.5%), and Ba (65%), suggesting that these HMs had a greater affinity with the finest fraction of the RDS (< 250 µm). Fe had the lowest affinity with this size fraction (see Table 4). Previous trend was probably associated with the particle size emitted by sources of HMs in the road environment. For example, Habibi (1973) reported that 43% of Pb emitted by vehicle exhausts was associated with particles sizes below 9 µm. Kobriger and Geinopolos (1984) informed that the action of tires generated the loosening of particles having an average diameter of 20 µm. Bannerman et al. (1993) and Li et al. (2001) showed that Zn in the tires of vehicles was a significant source of this metal in urban runoff. The dust embedded in the tires not only consisted of particles removed by their passage, but also HMs associated with particles emitted by traffic materials such as brake dust and roadway yellow painting (Adachi and Tainosho, 2004).

For the road surfaces studied, there was no significant correlation (Pearson's *r*, *p*-value > 0.05) between the HM-related pollution and the distribution of HM load in each size fraction of the RDS (see Table 4). The results suggested that the distribution of HMs in the different size fractions of the RDS was probably independent of pollution in the study area.

The level of pollution on road surfaces was evaluated by looking at HM concentration (mg/kg of dry matter) associated with RDS (see Table S1, Supplementary Information). On average, the concentrations of Pb, Zn, Cu, Cd, Fe, and Mn on the road surface of A1 were 2.00, 4.34, 2.16, 43.41, 0.16, and 2.49 times higher, respectively, than those of the A2 road surface (RDS size fraction < 250 µm). The results suggested that the study area with parking lanes (A1 road surface) presented the higher HM concentrations, probably due to a larger accumulation of grease, lubrication and motor oil on the sampling surface and to a greater use of the braking system, and greater wear of tires and asphalt as a result of the parking operations (see in Table 1, Traffic lines/parking). Moreover, in A1 and A2 the highest HM concentration occurred on the RDS size fraction below 63 µm. Therefore, the results suggested that the design of best management practices should be guided to eliminate the fine-size fraction of the RDS.

Table 5 shows a comparison of HM leaching in RDS observed in this study (DIN 38414-S4 standard) and that observed in other studies (Tessier and BCR sequential-extraction procedures). The leaching test allowed for the simulation of strong turbulent runoff conditions on RDS during storm drainage from the roadside surface (potential contribution). The leaching information in Table 5 corresponded to the water-soluble and exchangeable fraction of the RDS (percentage of bioavailable HM). The results did not show any significant differences between the results of the leaching tests for RDS in A1 and A2 (Student's *t*-test, *p*-value = 0.061). The evaluated HMs were Pb, Zn, Cu, Cd, Fe, and Mn. The results displayed no significant differences between the results of the leaching tests in this study and those reported in Table 5 by other studies (Student's *t*-test, *p*-value = 0.263). The evaluated HMs were Pb, Zn, Cu, Cr, Ni, Cd, Fe, Mn, and Co. However, Rijkenberg and Depree (2010) reported that the dissolved organic matter and pH were the most important solution parameters that affected the leaching of HMs from RDS. Therefore, in the present study, it was assumed a uniform behavior of these two parameters in stormwater runoff during the investigation period, due to the fact that the proposed method was based on the RDS collection of the same road surface. Namely, it was assumed that the influential factors in the HM leaching from RDS (e.g., chelating agents, rainfall pH, and sediment lithology) remained constant during the study period in each evaluated road surface.

The results of the HM leaching test for study areas A1 and A2 showed that the elements with the highest leaching percentages were Mn and Cd (Table 5). Based on averaged values, the sequence in leaching tests was: Mn > Cd > Zn > Cu > Ba > Pb > Co > Ni > Fe > Cr. Average leaching percentage for all HMs in A1 and A2 was 13.9% (Zn, Pb, Cu, Cr, Ni, Mn, Cd, Fe, Co, and Ba). The median leaching percentage for all HMs reviewed in RDS was 9.1%. The median was used as a central-tendency measure in light of the extreme values in the information reported in Table 5.

3.1.3. Development of the wash-off equation

The wash-off equation was:

$$\mathrm{TLW}=\sum_{\mathrm{i}=1}^{\mathrm{n}}\left[\left(\mathrm{LW}_{<250,\mathrm{i}}\cdot\frac{\mathrm{ML}_{<250,\mathrm{i}}}{100}\right)+\left(\mathrm{LE}_{<250}\cdot\left(1-\frac{\mathrm{LW}_{<250,\mathrm{i}}}{100}\right)\cdot\frac{\mathrm{ML}_{<250,\mathrm{i}}}{100}\right)\right]+\left(\mathrm{LE}_{\geq 250}\cdot\left(1-\frac{\mathrm{ML}_{<250}}{100}\right)\right) \qquad (1)$$

Where *TLW* is the potential load of HM washed-off by runoff from RDS (%), $LW_{<250,i}$ is the percentage of RDS under 250 µm susceptible to transport caused by runoff (see Table 3), $ML_{<250,i}$ is the percentage of HM associated with RDS under 250 µm (see Table 4), $LE_{<250}$ is the percentage of HM leaching associated with RDS under 250 µm (see A1 and A2 in Table 5), and $LE_{\geq 250}$ is the percentage of HM leaching associated with RDS greater than or equal to 250 µm (see median for each HM in Table 5). The term $(1\text{-}LW_{<250,i}/100)$ represents the proportion of RDS under 250 µm that was not transported by runoff yet leached HMs. *TLW* depends on the number of fractions under 250 µm, which is considered (*n*). A second term was included to quantify the potential HM contribution for size fractions greater than or equal to 250 µm, assuming that this size fraction was not susceptible to transport but rather leached by road runoff. The term $(1\text{-}ML_{<250}/100)$ indicates the proportion of an HM associated with this RDS size fraction. As noted, the wash-off equation was developed using the data reported in Tables 3, 4, and 5.

The potential load of HMs (Pb, Zn, Cu, Cr, Ni, Cd, Fe, Mn, Co, and Ba) derived from wash-off caused by runoff on RDS was calculated using the equation developed for the simplified method. Figure 1 shows the results obtained for the potential load of HMs attributable to RDS runoff. On average, 27.2 and 37.2% of the total HM load associated with RDS was susceptible to wash-off after a rainfall event for A1 and A2, respectively. In order of precedence, the average load for each HM at A1 was (Figure 1): Cd > Mn > Zn > Co > Cu > Pb > Ni > Cr and Fe. At A2, the order of precedence was: Cd > Zn > Mn > Ba > Cu > Pb > Fe. The HMs that contributed the most to the road surfaces studied were: Cd (43.7%), Mn (41.4%), and Zn (40.3%). Detailed results for each variable and term of the wash-off equation are available in Table S2 (Supplementary Information).

For the road surfaces studied, no significant correlation (Pearson's *r*, *p*-value > 0.05) was found between pollution caused by HMs and the HM load caused by runoff (calculated using the proposed equation), for HM load was calculated with respect to the total mass of HM associated with the dry-weather RDS at each study site. The results suggested that the wash-off equation developed was probably independent of pollution levels in the RDS, which meant that the equation could be applied to road surfaces with different land uses and HM-related pollution levels. Pollution on the road surfaces was evaluated with regard to the HM concentration (mg/kg of dry matter) associated with RDS (Table S1, Supplementary Information). Moreover, no significant correlation (Pearson's *r*, *p*-value > 0.05) was found between HM load caused by runoff (calculated using the proposed wash-off equation) and the following variables: rainfall intensity, ADP, and road slope. However, a direct relationship between these variables was observed in Figure 1. For example, for the A1 and A2 road surfaces, rainfall intensities between 0.8-3.7 mm/h and 0.8-4.5 mm/h were correlated with an average HM load caused by runoff of 27.2 and 37.2%, respectively. As noted, increased rainfall intensity led higher average HM load (calculated with the wash-off equation).

Potential HM load was evaluated using the equation proposed as part of the simplified method. For A1 and A2, an average of 86.8 and 86.5%, respectively, of potential HM load washed-off by runoff came from the size fraction under 250 µm (Figure 1). This was integrated in the HM-related phenomena included in the first term of the developed equation (Equation 1): transport of RDS < 250 µm (solid fraction) and leaching of RDS <

250 µm (dissolved fraction). Similarly, Zhao et al. (2010) reported that this size fraction contributed more than 80% of total HM load washed-off by runoff from RDS.

The size fraction greater than or equal to 250 µm accounted for an average HM load of 13.2% for A1 and 13.5% for A2, relative to total HM-load wash-off caused by runoff from RDS (Figure 1). This was integrated in the only phenomenon included in the second term of the developed equation (Equation 1), namely leaching of RDS ≥ 250 µm (dissolved fraction). Thus, the proposed equation allowed us to visualize the following order of precedence: transport of RDS < 250 µm (70.7%), leaching of RDS < 250 µm (15.9%), and leaching of RDS ≥ 250 µm (13.4%). On average, in this study, solid and dissolved fractions contributed 70.7 and 29.3% of the potential HM load washed-off by stormwater runoff from RDS, respectively.

As noted, our wash-off equation did not depend directly on the study areas' climate conditions (e.g., rainfall intensity and ADP) or physical characteristics (e.g., road slope and curbs). Formulation of the equation depended on the transport and leaching processes exerted by the surface runoff on RDS. Therefore, we suggest applying the simplified method described in this paper to any sampling or collection system of dry-weather RDS.

3.2. Validation of the simplified method

Table 6 contains a review of other studies on HMs. Initially, we validated the results obtained via the simplified method (potential conditions) by comparing them with the results of other studies (real conditions). As expected, the comparison revealed that the simplified method for potential HM load tended to overestimate the HM load relative to the values reported in other studies by an average of 55.2, 112, 116, 126, 50.1, 179, 125, and 266% for Pb, Zn, Cu, Cr, Ni, Cd, Fe, and Mn, respectively (a combined overestimation average of 129%). This overestimation of potential HM load was probably due to the fact that, in the proposed wash-off equation, strong turbulent runoff conditions were considered for the RDS (laboratory leaching tests: DIN 38414-S4 standard, and Tessier and BCR sequential-extraction procedures). It is unlikely that all HMs leached in the laboratory would leach with the same intensity during rainfall events. Previous comparisons with other studies were useful for validating the proposed simplified method.

The simplified method was also validated in comparison to the simulated (potential conditions) and observed (real conditions) values for A1 and A2 road surfaces. Figure 2 shows the results for study section A11. Results for the other sections studied can be found in Figures S1, S2, and S3 (Supplementary Information). As expected, the results revealed that the simplified method tended to overestimate the HM load wash-off observed for A1 and A2 road surfaces for the 19 rainfall events that occurred during the study period. For A1, an overestimation average of 54.8, 100, 37.6, 38.0, 76.4, 49.2, 41.0, 120, 50.3, and 63.0% was found for Pb, Zn, Cu, Cr, Ni, Cd, Fe, Mn, and Co, respectively (with a combined overestimation average of 63%). For A2, an overestimation average of 50.9, 86.8, 65.9, 92.5, 66.9, 71.4, and 66.8% was found for Pb, Zn, Cu, Cd, Fe, Mn, and Ba, respectively (with a combined overestimation average of 71.6%). Finally, to simulate the potential HM load under average conditions (i.e., for all rainfall events), we found that 85.2 and 90.1% of the observed values were lower than the average values simulated for A1 and A2, respectively (Figure 2).

4. Conclusions

In this study, we propose a simplified method for determining the potential load of HMs derived from wash-off caused by runoff on RDS. This study's findings allow us to draw the following conclusions.

Results obtained using the simplified method suggest that the potential load of HMs washed-off by runoff from RDS averaged between 16.6 and 46.3% (for the following HMs: Mn, Cd, Zn, Cu, Ba, Pb, Co, Ni, Fe, and Cr), with percentages relative to the total mass of HMs associated with dry-weather RDS. The HMs with the highest wash-off are: Cd, Mn, and Zn. These HMs consistently show the highest percentages of leaching in laboratory tests. Based on the phenomena included in the wash-off equation, we observed the following order of precedence: transport of RDS < 250 μm (solid fraction), leaching of RDS < 250 μm (dissolved fraction), and leaching of RDS ≥ 250 μm (dissolved fraction). The size fraction under 250 μm contributes an average of 86.7% of potential HM load washed-off by runoff from RDS; the remaining 13.3% is contributed by the RDS size fraction greater than or equal to 250 μm. Solid and dissolved fractions contribute 70.7 and 29.3% of the potential HM load washed-off by runoff from RDS, respectively. On average, for potential conditions of HM load wash-off, the simplified method tends to overestimate the HM load wash-off observed on the road surfaces by a factor of 63 to 71.6%.

Finally, the simplified method may serve as a management tool for institutions responsible for controlling diffuse pollution in urban areas. That is, it may help establish control strategies for dry weather, i.e., optimizing the frequency/schedule for street sweeping, and for wet weather, i.e., optimizing permeable/porous pavement design, infiltration/exfiltration trenches and basins, and retention/detention ponds, etc. The design for polluted runoff should be guided to eliminate the fine-size fraction of the RDS (e.g., < 250 μm). Therefore, this method can improve future research on the influence of rainfall events in relation to the HM loads washed-off by runoff from RDS.

However, this study had the following limitations, which require further attention. First, the wash-off equation was developed in strong turbulent runoff conditions. It is unlikely that all HMs leached in the laboratory (potential conditions) would leach with the same intensity during rainfall events (real conditions). Second, the simplified method was developed under specific conditions, such as climate, physical road and asphalt surface, rainfall intensity (0.8 to 3.7 mm/h), ADP (1 to 27 days), road slope (0.2 to 4%), and HM leaching (DIN 38414-S4 standard). These specific conditions do not apply to all RDS situations, and, as we have pointed out in this paper, discrepancies in these variables may lead to discrepancies in the results of the simplified method. Third, specific conditions during method development (i.e., land use and road-traffic density and composition) were shown to determine HM-related pollution for the road surfaces studied.

Conflict of interest

The authors declare that there are no conflicts of interest.

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