Metal size distribution in rainfall and snowmelt-induced runoff from three urban catchments

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HIGHLIGHTS

- Dissolved metal concentrations are dominated by the truly dissolved fraction.
- Truly dissolved metals contribute 1% (Cr) - 28% (Zn) of total metal concentrations.
- Particulates are unlikely the only source of truly dissolved or colloidal metals.
- Metal concentrations per fraction did not indicate a seasonal or site variation.

GRAPHICAL ABSTRACT
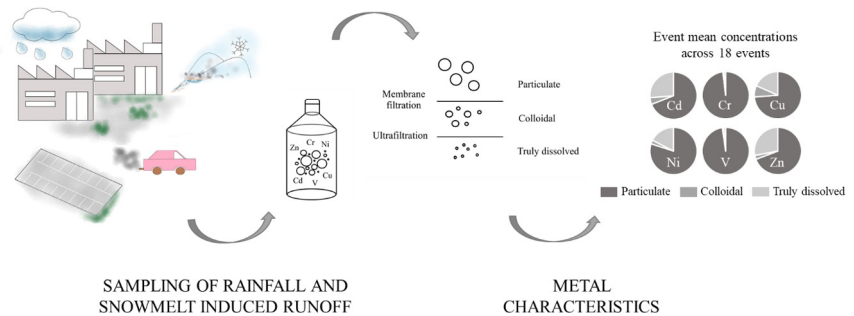
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ABSTRACT

The size distribution of metals transported by urban runoff has implications for treatment type and design, predicting their mobility and evaluating their potential impact on receiving waters. There is an urgent need to better understand the distribution of metals between fractions, particularly those in the sub-dissolved fractions. As a contribution to addressing this need, this study characterises the size distribution of Cd, Cr, Cu, Ni, V and Zn using conventional and novel techniques. Data is presented as event mean concentrations (EMC) of a total of 18 rainfall and snowmelt events at three urban sites. For all studied metals in all events and at all sites, the contribution of the truly dissolved fraction made a greater contribution to the total concentrations than the colloidal fraction. Truly dissolved Cd and Zn concentrations contributed (on average) 26% and 28% respectively, of the total EMCs with truly dissolved Cu and Ni contributing (on average) 18%. In contrast, only 1% (V) and 3% (Cr) were identified in the truly dissolved fraction. The greatest contribution of truly dissolved Cd, Cu and Zn concentrations (relative to total concentrations) were reported during rainfall events. However, no seasonal differences were identified and differences between the sites regarding the EMCs distribution by fractions were not at a statistically significant level (p > 0.05) for any metal or event. The loads of truly dissolved and colloidal metals did not follow the patterns of particulate metal loads indicating particulates are not the main source of sub-dissolved metals. The data suggests that ultrafiltration as a treatment technique would not efficiently mitigate the risks posed by metals to receiving water ecologies.

1. Introduction

Urban runoff is a major pathway for the transportation of non-point source pollution, contributing a range of contaminants (including metals, pesticides, polyaromatic hydrocarbons (PAHs) and bacteria) to receiving waters (Eriksson et al., 2007; Makepeace et al., 1995). These

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originate from a diversity of sources such as traffic, building materials and the atmosphere (e.g. Müller et al., 2020). The distribution of metals between different size fractions affects their environmental fate by, for example, influencing the potential for processes such as physical and/ or chemical sorption to particulate matter to occur and their subsequent sedimentation (O'Melia and Tiller, 1993).

Standard practice for the analysis of pollutants mobilised by runoff involves subdividing collected samples into dissolved and particulate fractions, operationally defined by filtration through a filter with a pore size of 0.45 μm (Buffle et al., 1992). Several studies have shown that the dissolved fraction can be further sub-divided into colloidal and truly dissolved fractions (e.g. Gustafsson and Gschwend, 1997; Ross and Sherrell, 1999; Stumm and Morgan, 1996) define colloids as dynamic complexes in a size range between 1 nm and 1 μm in at least one dimension.

The truly dissolved fraction, which is the smallest size fraction herein defined as <3000 molecular weight cut off (3 kMWCO), mainly consists of hydrolysed ions that are typically considered as bioavailable (Morel, 1983; Sunda and Guillard, 1976). Knowledge of the behaviour of metals in sub-dissolved fractions in urban runoff is currently limited. However, development of a full understanding of the urban hydro-geochemistry is critical in order to enable environmental impacts to be predicted, support sustainable water resources management and protect public health (Guo et al., 2000; Martin et al., 1995; Ure and Davidson, 2002; Waeles et al., 2008; Wong et al., 2012).

Depending on environmental conditions, urban runoff has been shown to exhibit toxicity to both marine and freshwater species where the primary cause of toxicity was subscribed to cationic metals, mainly Cu and Zn (Kayhanian et al., 2008). Several metals, including Cd, Cr, Cu, Ni, and Zn was included in the stormwater priority pollutants list suggested by Eriksson et al. (2007) due to their prevalence in urban runoff and inclined toxicity in receiving environments. Vanadium, even though recieved much less attention, was included in this study motivated by its occurence in typical urban runoff sources such as asphalt and brake dust (Mummullage et al., 2016) and its reported toxicity in surface water conditions (Gillio Meina et al., 2019; Schiffer and Liber, 2017).

The distribution of metals between colloidal and truly dissolved fractions in watercourses has been shown to be influenced by land-use (Grout et al., 1999; Guéguen and Dominik, 2003; Jarvie et al., 2012). For example, a study by Grout et al. (1999) indicated a shift towards higher colloidal Cr and Zn concentrations in an urban waterway during a storm event. McKenzie and Young (2013) reported that highway and urban runoff contributed higher concentrations of truly dissolved metals (defined as the <10 kDa fraction) compared to concentrations of the same fraction reported within agricultural runoff during event peak flow. The higher concentrations of truly dissolved metals were suggested to originate from transportation sector sources.

Seasonal changes have also been identified as affecting the distribution between particulate and dissolved metal phases (McKenzie and Young, 2013). For example, research by Glenn and Sansalone (2002) showed that the dissolved metal fraction in highway runoff were lower during snowmelt conditions in contrast to summer sampling undertaken at the same sites in Cincinnati (Ohio, USA) with the authors suggesting this to be due to the longer pavement residence time during snowmelt, which allowed for colloids to aggregate. In contrast, seasonal road runoff in Sweden (Westerlund et al., 2003) and Germany (Helmreich et al., 2010) showed no significant difference (p > 0.05) between the dissolved metal fractions in rainfall runoff compared to snowmelt runoff.

Previous studies on cold season characteristics of colloidal and truly dissolved metal fractions in urban runoff are limited. However, one example is a study by Morrison and Benoit (2005) which reported the metal distribution in an urban river (Torrington, CT, USA) during a winter rain-on-snow event. Under peak flow conditions, the data indicated a change in distribution from primarily truly dissolved metals, defined

as <3 kMWCO, during pre-flow conditions towards a higher percentage of colloidal metals during the event.

To the authors' knowledge, the distribution of metals between colloidal and truly dissolved fractions under differing seasonal variations in runoff from well-defined urban areas has yet to be investigated. As a contribution to addressing this identified data gap, this paper presents results of rainfall, snowmelt and rain-on-snow runoff sampling campaigns which involved the determination of the total, particulate (>0.45 μm), colloidal (0.45 μm - 3 kMWCO) and truly dissolved (<3 kMWCO) metal concentrations in three urban catchments; two industrial parks and one parking lot. The pore size of <3 kMWCO defines compounds in the truly dissolved fraction as less than ~1 nm in size (Lead and Wilkinson, 2006). For the first time in an urban runoff context, a rapid and cost effective ultrafiltration method was used to operationally identify metals in the truly dissolved fraction. The aim of this study was to characterise the distribution of colloidal and truly dissolved fractions of Cd, Cr, Cu, V and Zn from different land uses and investigate if there are seasonal differences in identified metal distributions. EMCs and mass loads are calculated for the different event types both within and between sites. It is within this context that this research contributes to both the development and assessments of contamination sources and the evaluation of implications for runoff treatment.

2. Material and methods

2.1. Site description

Runoff from three urban catchments in Umeå, northern Sweden, were investigated, see Fig. 1. Umeå experience an annual average temperature of 3 degrees Celsius and an annual average rainfall depth of 700 mm. Two of the studied sites were industrial parks (identified as IP1 and IP2) and the third site collected runoff from a parking lot (PL) next to a hospital. The two industrial parks had total catchment areas of 15 ha and 12 ha, with approximately 75% and 85% levels of imperviousness, respectively, composed of coated corrugated steel and bitumen sheet roofs and asphalt pavement. IP1 and IP2 were drained by a pipe network consisting of concrete pipes with groundwater infiltration generating a base flow at both sites. The activities within IP1 and IP2 consisted mainly of light industries (construction, car and transport services), together with offices and commercial activities. Annual average traffic density was approximately 8000 vehicles/day on the main road of IP1 and 3000 vehicles/day on a road leading to IP2. The parking lot's 0.45 ha catchment was composed of impervious asphalt (95%) and green areas (5%), with plastic pipes and no baseflow or connections of roof runoff from surrounding buildings. The annual daily traffic density was 1630 vehicles/day for the road adjacent to PL. Traffic density at the actual parking lot was assumed to be approximately six and thirteen times higher than at IP1 and IP2, respectively, based on this observation and the catchment sizes.

2.2. Sampling methods and sampled events

Automatic water samplers (ISCO, 6712 Portable Sampler) with 24 bottles of 1 L (polypropylene; ISCO) were used to collect volume proportional samples at each site. Area-velocity flowmeters (ISCO, 2150 AV) recorded flow volume at one minute intervals during runoff events. Sample tubing (PVC) together with the flowmeter was mounted at the bottom of each stormwater pipe upstream of a manhole. At the sites with base flow, accumulated sediments and precipitations were cleared before each sampling event and the sample tubing was automatically rinsed prior to each sample being collected. Sampling frequency was programmed for each event with a minimum of five volume proportional samples collected (based on a combined assessment of the weather forecast and calculation of the anticipated runoff volume generated). After collection of the fifth sample, the sampling frequency was reduced by half to enable the profile of longer events to be covered.
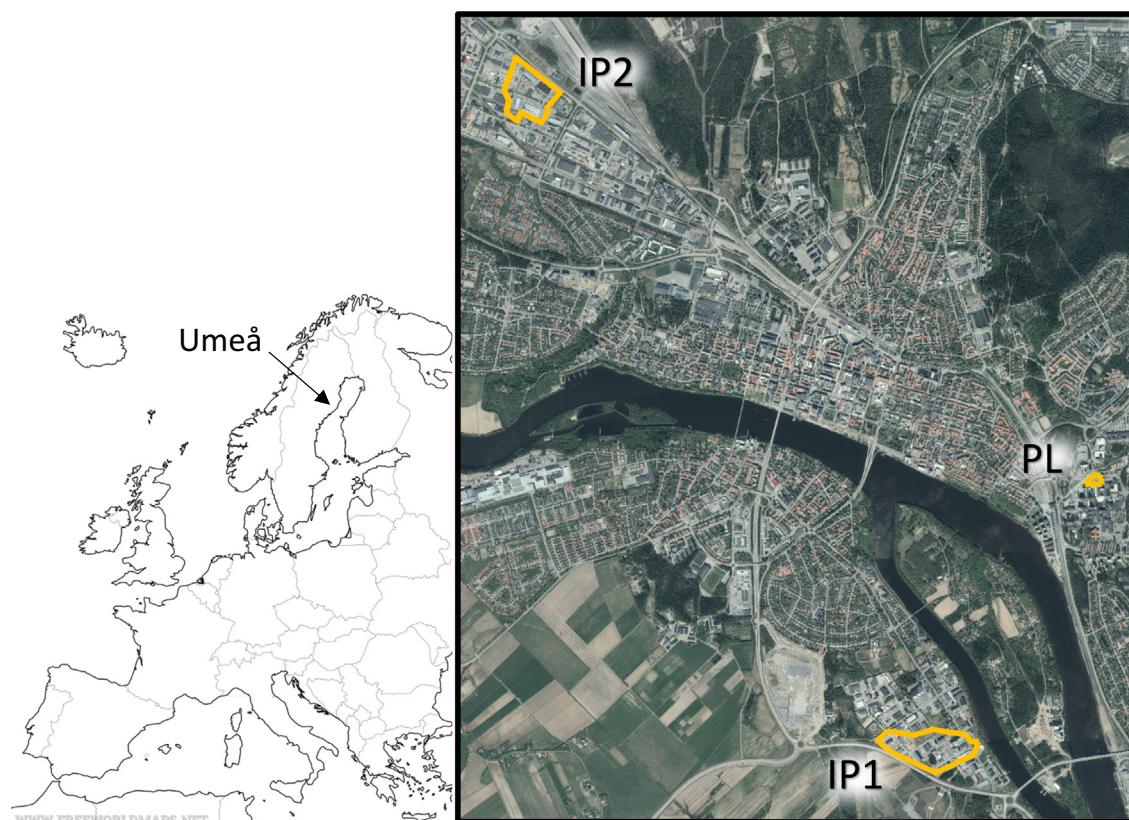
Fig. 1. Map over the sampled catchments IP1, IP2 and PL in Umeå, northern Sweden.

The number of samples varied from 5 to 13 for all events and sites. Sample bottles were placed in cooler bags, transported to the university laboratory and analysed for physicochemical parameters and subjected to filtration (<0.45 μm) and ultrafiltration (<3 kMWCO) within 24 h of the last sample being collected.

Table 1 presents an overview of the characteristics of seven monitored precipitation events during 2016 and 2017. On seven dates, at three sites, a total of 18 events were sampled. Data reported demonstrated the characteristically variable nature of runoff events in terms of, for example, event duration (e.g. between sites on the same date) and flow rate (for example, flow rate varied by up to three orders of magnitude within an individual event). Antecedent dry periods ranged from two and three days for the second and third rainfall event (RF2 and RF3) respectively, up to six days for rainfall event 1 (RF1). RF3 occurred after the first frost in autumn of 2017 and following the application of antiskid materials (grit; which otherwise is characteristic for snowmelt events). The season old snowpack melting during snow melt event 1 (SM1) was approximately 5 cm in depth including a light snowfall occurring two days preceding the sampling occasion. Antecedent conditions for snowmelt events in spring 2017 (SM2 and SM3) are similar to each other; a season old snowpack, approximately 30 cm in depth with a small addition of snow mixed with rain one week prior to SM2 and one day prior to SM3. A week prior to the rain on-snow event (RoS) in November 2016, there was a snowfall leaving approximately 10 cm of snow on the ground. During the RoS, the snow was exposed to melting degrees and a 3-hour rainfall event with an average intensity of 1.5 mm/h.

2.3. Fractionation and analysis

All samples were processed to identify the total, dissolved (<0.45 μm), and truly dissolved (<3 kMWCO) fractions (Fig. 2). Samples were filtered using 0.45 μm membrane syringe filters (Sarstedt, Filtropur S 0.45), and the filtrate directly injected into 20 mL ultrafiltration centrifugal columns

(Sartorius, Vivaspin 20, 3000 MWCO PES membrane) which were then centrifuged at 4000 rev/min (Eppendorf, Centrifuge 5804) for 50 min. The colloidal fraction was calculated as the difference between the dissolved and truly dissolved concentration (i.e. the 0.45 μm - 3 kMWCO fraction) and the particulate fraction as the difference between total and dissolved concentrations (i.e. the >0.45 μm fraction). The use of centrifugal columns to estimate the truly dissolved fraction allowed for up to 16 samples to be processed within an hour and only required the aid of a centrifuge. In addition, the centrifugal columns are affordable (approximately 14 euro/15 USD per unit), though only for one time use.

Procedural blanks consisting of deionised water were subjected to the same procedure for every event. Total suspended solids (TSS) were determined according to SS-EN 872: 2005 with use of a sample aliquot and a dried and pre weighted glass microfibre filter (Whatman, GE Healthcare, GF/A 1.6 μm pore size and 53 g/m2). pH was recorded with a calibrated WTW pH 330 device (WTW, Weilheim,Germany) and turbidity measurements were conducted using a Hach Turbidimeter 2100N (Hach, Loveland, CO, USA). A CDM210 conductivity meter (Radiometer, Copenhagen, Denmark) was used to determine electrical conductivity. Samples were kept at 4 °C before delivery to an accredited laboratory (ALS Scandinavia, Luleå, Sweden) for metal analyses, including full quality assurance and quality control procedures. Samples were digested in 1.3 M nitric acid in an autoclave for total concentrations and acidified in 0.14 M nitric acid for analysis of dissolved and truly dissolved concentrations. Concentrations of Cd, Cu, Cr, Ni, V and Zn were determined using both inductively coupled plasma sector field mass spectrometry (ICP-SFMS) and optical emission spectroscopy (ICP-OES) according to SS EN ISO 17294-2:2016 and 11885:2009, respectively. In general, Cu and Zn concentrations were reported from analysis of ICP-OES, whereas Cd, Cr, Ni and V were reported from analysis of ICP-SFMS.

Volume weighted event mean concentrations (EMCs) of metals and TSS were calculated as in Leecaster et al. (2002) for each sampling site and event according to the equation:

Table 1
Overview of rainfall event characteristics.

Event dates	Event characteristics	Industrial park 1 [IP1]	Industrial park 2 [IP2]	Parking lot [PL]
RF1: 16/6/16	Event duration	5 h 45 min	5 h 11 min	5 h 59 min
	Minimum-maximum flow rates [l/s]	4.11–95.8	0.12–143	0.001–12.97
	Mean flow rate ± SD [l/s]	38.1 ± 23.9	24.0 ± 25.3	2.06 ± 2.03
	Total runoff volume [m³]	711	444	38
	Runoff intensity [l/s/m²]	2.29	1.98	3.89
	Rainfall depth [mm][a]	7.4	10.4	7.4
RF2: 02/10/17	Event duration	12 h 51 min	14 h 58 min	14 h 55 min
	Minimum-maximum flow rates [l/s]	2.03–131	0.11–92.6	0.01–6.74
	Mean flow rate ± SD [l/s]	49.6 ± 39.8	32.2 ± 26.6	2.09 ± 2.03
	Total runoff volume [m³]	2032	1521	92
	Runoff intensity [l/s,m²]	2.93	2.35	3.83
	Rainfall depth [mm][a]	14.8	19.4	14.8
RF3: 09/11/17	Event duration	13 h 23 min	14 h 12 min	No data
	Minimum-maximum flow rates [l/s]	2.68–81.9	0.30–57.9	
	Mean flow rate ± SD [l/s]	35.4 ± 24.4	21.2 ± 14.1	
	Total runoff volume [m³]	1453	925	
	Runoff intensity [l/s/m²]	2.01	1.51	
	Rainfall depth [mm][a]	9.2	9.2[b]	
SM1: 25/4/16	Event duration	17 h 7 min	20 h 12 min	12 h 52 min
	Minimum-maximum flow rates [l/s]	4.04–41.30	0.64–14.40	0.01–2.07
	Mean flow rate ± SD [l/s]	22.0 ± 11.60	8.50 ± 3.79	0.80 ± 0.50
	Total runoff volume [m³]	1287	560	40
	Runoff intensity [l/s/m²]	1.39	0.64	1.92
SM2: 16/3/17	Event duration	10 h 53 min	17 h 39 min	No data
	Minimum-maximum flow rates [l/s]	3.91–52.90	1.69–15.04	
	Mean flow rate ± SD [l/s]	23.0 ± 13.1	6.07 ± 3.69	
	Total runoff volume [m³]	836	377	
	Runoff intensity [l/s/m²]	1.42	0.49	
SM3: 22/3/17	Event duration	9 h 28 min	No data	11 h 5 min
	Minimum-maximum flow rates [l/s]	3.27–45.20		0.001–2.06
	Mean flow rate ± SD [l/s]	22.4 ± 10.6		0.47 ± 0.45
	Total runoff volume [m³]	704		13
	Runoff intensity [l/s/m²]	1.38		0.74
RoS: 14/11/16	Event duration	23 h 21 min	23 h 47 min	21 h 35 min
	Minimum-maximum flow rates [l/s]	3.83–128	1.40–43.3	0.01–4.14
	Mean flow rate ± SD [l/s]	33.2 ± 30.5	13.9 ± 11.2	0.68 ± 0.97
	Total runoff volume [m³]	2577	1011	42
	Runoff intensity [l/s/m²]	2.04	0.98	1.21
	Rainfall depth [mm][a]	12.6	9.8	12.6

[a] Rainfall depth was recorded at two stations, station 1 was within 500 m from IP1 and 1.5 km from PL, station 2 was within the catchment of IP2.
[b] Station 2 was not operating during RF3, data from station 1 presented.

$$EMC = \frac{\sum_{i=1}^{n} C_i * V_i}{\sum_{i=1}^{n} V_i}$$

where C_i is the concentration of sample i among n number of samples multiplied with V_i, the runoff volume associated with sample i and divided by the total volume $\sum_{i=1}^{n} V_i$. The sample associated volume is defined as half the volume between sample i-1 and i, plus half the volume between sample i and i+1. Statistical analysis by ANOVA, t-test and linear regression was used to compare the metal EMCs in the measured fractions for the different event types and sites as well as correlation with water quality parameters.

3. Results and discussion

3.1. Event characteristics

The event characteristics, presented in Table 1, showed that snowmelt events in general generated lower total runoff volumes,
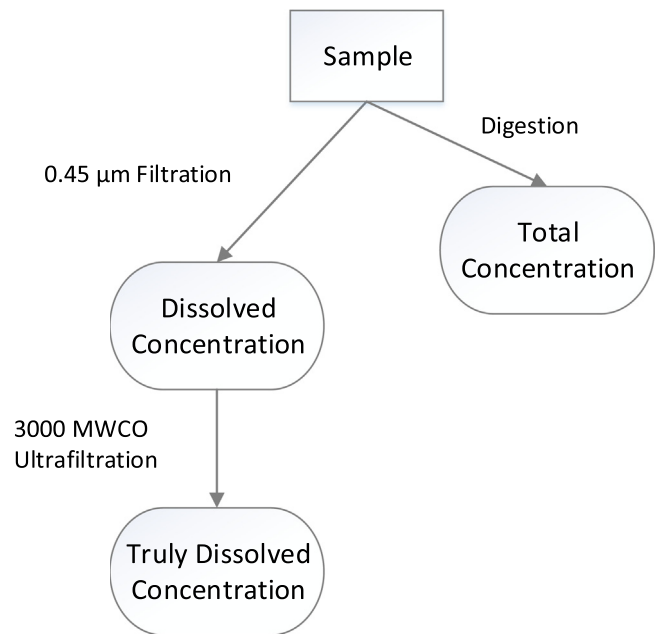

Fig. 2. Operational processing for metal fractions.

and mean and maximum flow rates compared to rainfall events. However, the highest runoff volume was recorded during the rain on-snow event (2577 m³; see Table 1), with the same trend also described by Westerlund et al. (2003). As anticipated, runoff volume generated per event and event type, decreased in the order of decreasing catchment size. However, despite identified variations in event parameters, the runoff intensity (l/s/m2) showed less variation (typically less than twice the value per site per event type) suggesting that, catchment response was predictable for each site and event type.

3.2. Physicochemical parameters

EMC values of general water quality parameters are presented in Table 2. Conductivity levels (ranging from 0.94–76.6 mS/m) were highest at the parking lot during SM and RoS events, understood to be associated with the fact that antiskid materials containing salts were frequently applied to this heavily used site. Whilst concentrations of TSS, turbidity and conductivity varied, sometimes over an order of magnitude, between sites and type of event (e.g. 54–1320 mg/L TSS, 25–1575 NTU and 0.94–51 mS/m in RF2 and SM3 respectively at PL), analysis of data using ANOVA did not indicate that any identified trends were statistically significant ($p > 0.05$).

These results contrast with those of a study on seasonal variations in road runoff quality which concluded that concentrations of TSS were higher in snowmelt runoff than during rainfall events (Westerlund et al., 2003), with elevated loads associated with the accumulation of available materials within snow over time. A reason for the absence of seasonal differences within this study could be that the runoff samples were taken within the pipe system after sediment traps which affect the TSS concentrations, compared to Westerlund et al. (2003) where runoff was collected directly at the drain inlet before any treatment. The pH values reported (5.97–7.57) were within the range of those previously reported in urban runoff (pH: 4.5–8.7) (e.g. Makepeace et al., 1995; Viklander, 1997) with both the lowest and highest pH values noted at PL. Similar to previous studies (Galfi et al., 2016; Helmreich et al., 2010; Sansalone et al., 1996) pH values did not vary by season, Harrison and Wilson (1985) suggested that this could be due to the buffering action of minerals, such as $CaCO_3$, deriving from antiskid materials.

Table 2
Overview of EMCs for selected physicochemical parameters per site for seven monitored events.

Event	RF1			RF2			RF3		SM1			SM2		SM3		RoS		
Site	IP1	IP2	PL	IP1	IP2	PL	IP1	IP2	IP1	IP2	PL	IP1	IP2	IP1	PL	IP1	IP2	PL
No. samples	7	6	8	13	12	11	6	8	12	12	11	7	5	7	6	12	9	6
Conductivity (mS/m)	8.84	8.10	3.20	3.63	4.83	0.94	8.82	6.81	8.63	10.1	28.7	54.7	41.4	16.8	51.2	17.9	18.7	76.6
pH	6.42	6.37	5.97	6.89	6.75	6.82	6.82	6.78	6.57	6.48	6.75	6.97	6.74	6.91	7.57	6.63	6.63	7.03
Total suspended solids (mg/l)	173	670	115	148	99.8	35.1	268	147	190	49.8	158	261	209	341	1320	164	84.7	289
Turbidity (NTU)	613	292	99.9	166	80.8	25.0	414	162	1929	68.4	178	320	164	513	1575	241	86.6	437

3.3. Total and particulate metal EMCs

A total of 18 separate events were monitored across the three sites, and total, dissolved and truly dissolved EMCs for Cd, Cr, Cu, Ni, V and Zn are presented in Table 3. Total metal concentrations ranged (in μg/L) for Cd: 0.05–0.37, Cr: 3.08–252, Cu: 10.7–134, Ni: 1.93–99.9, V: 3.69–186 and Zn: 54.3–537 and, disregarding V, were within the range of those previously reported in urban runoff, Cd: 0–5 and Cu: 1–205 (Revitt et al., 2014) and Cr: 0.06–222, Ni: 0.66–122 and Zn: 7.3–1937 μg/L (Valtanen et al., 2014). With regard to rainfall events, two of the three events (RF2 and RF3) for all metals but Cd showed a pattern of decreasing total EMCs with decreasing catchment size. For example total Zn concentration during RF2 ranged from 54.3 μg/L at PL to 82.1 μg/L at IP2 and 194 μg/L at IP1, see Fig. A, supplementary material. During RF1, metal concentrations measured at IP1 were higher than at PL but the highest metal concentrations were measured at IP2. This could be due to RF1's longer antecedent dry period and the higher percentage of impervious areas at IP2 compared with IP1.

During the two SM events and RoS at the smallest catchment, PL, total EMCs were continuously higher than at IP2 and on a number of occasions exceeded total EMCs at IP1 (on three occasions for Cd, Cr, and Ni, twice for Cu and V and on one occasion for Zn). These patterns for SM and RoS events are not consistent with those identified for RF events. This could be due to a dilution effect at site IP1 and IP2 during winter (when melting pristine snow from large green areas were discharged into the pipe system together with contaminated snowmelt) in contrast to events during the warm season (when the green areas did not generate as much runoff due to infiltration). The fact that PL has a low degree of green areas and a major part of the catchment was regularly treated with antiskid material could explain the reported higher total EMCs at PL compared to IP1 and IP2 during SM events.

Despite the trends seen between the sites, ANOVA tests showed no statistical significant differences (p > 0.05) for total metal EMCs between the sites for any event type. Highest total EMCs for all metals were measured during SM3 at PL, e.g. 134 μg/L for Cu and 538 μg/L for Zn, and lowest total metal EMCs were observed in the same catchment during RF2 for all metals, e.g. 10.7 μg/L for Cu and 54.3 μg/L for Zn. Minimum and maximum TSS EMCs, 35.1 mg/L and 1319 mg/L, were reported in the same samples as for lowest and highest total metal EMCs, respectively, indicating a relationship between total metal concentrations and TSS.

The samples with minimum and maximum particulate EMCs for all metals but Cd were reported at PL in RF2 and SM3, respectively, data not presented. This is consistent with the data for total EMCs, indicating that sources of particulate matter influence the total concentrations of metals present. It is also an indication of a seasonal pattern (higher concentrations in the particulate fraction during SM events compared to RF events). However, this trend did not occur at a level that was statistically significant (p > 0.05). Looking at the whole dataset, particulate EMCs of all metals in this study were statistically significantly higher (p < 0.05) than dissolved concentrations. This was consistent regardless if dividing the data into the different event types. In Glenn and Sansalone (2002), the particulate metal concentrations exceeded dissolved metal

concentrations during SM events but not during RF events. This was explained by shorter pavement residence time during rainfall compared to snowmelt events as a longer residence time would enable more dissolved metals to adsorb onto highway solids (Glenn and Sansalone, 2002). However, Valtanen et al. (2014) reported Ni and Cr concentrations to be greater in the particulate as compared to the dissolved fraction during a RF event. Furthermore, e.g. Westerlund et al. (2003) reported that no statistical difference (p > 0.05) was found in the distribution of particulate and dissolved EMCs per metals between seasons. This lack of consistency in distribution of metals between the particulate and dissolved phase during seasons indicate further research is required before governing factors can be fully understood.

Previous studies have not been able to reveal a significant seasonal difference for all measured constituents. However, Westerlund et al. (2003) reported significantly higher (p < 0.05) suspended solids and total concentrations of Cd and Cu in road runoff during the SM period compared to RF events, and no significant difference in Zn and Ni concentrations by event type. During a two year study of road runoff in Germany by Helmreich et al. (2010), results indicated a significant (p < 0.05) seasonal difference with higher total Zn and Cu concentration during the melt season whereas only a slight seasonal variation was seen for Cd, Ni and Pb. In this study, total EMCs for all metals did not significantly differ (p > 0.05) between event types (RF – 8 EMCs and SM – 10 EMCs including RoS) however, there was a trend observed with highest total metal EMCs recorded in snowmelt and lowest in rainfall. Factors identified which could contribute to increased pollutant levels reported during the SM period events include increased road and tyre wear as a function of snow clearing activities which scrape snow from road surfaces (generating road fragments), the use of tyre studs (reported to degrade road surfaces) and the application of antiskid materials (increasing friction between tyres and road materials) (Helmreich et al., 2010; Westerlund et al., 2003). Further factors include the accumulation of pollutants in snowbanks over extended time periods, with elevated TSS loads reported providing available binding sites for metals and storage within snow banks, enhancing opportunities for adsorption to particulate matter with a subsequent and relatively rapid released during the snowmelt (Westerlund et al., 2003).

3.4. Dissolved, truly dissolved and colloidal metal EMCs

Results of this study indicate that on average 28% of Cd (range: 3–76%), 1% of Cr (range: 0.1–10%), 19% of Cu (range: 4–51%), 18% of Ni (range: 2–41%), 3% of V (range: n/a-22%) and 29% of Zn (range: 1–64%) total EMCs occurred in the truly dissolved fraction (n/a represents EMCs that falls below the concentration in the blank sample), see Fig. 3. These results indicate a need for runoff characterisation to inform the selection of treatment technologies on the basis of their ability to target the fraction that is understood to have the greatest ecological impact.

In terms of relative contribution, samples with the lowest concentration in the truly dissolved fraction (as a percentage of total EMC) were found at PL during SM3 for all metals with the exception of V. The

Table 3
EMCs for Cd, Cr, Cu, Ni, V and Zn in the analysed fractions total, dissolved and truly dissolved (Tr. dissolved) per site and seven monitored events.

Event Site	Fraction	RF1 IP1	RF1 IP2	RF1 PL	RF2 IP1	RF2 IP2	RF2 PL	RF3 IP1	RF3 IP2	SM1 IP1	SM1 IP2	SM2 IP1	SM2 IP2	SM3 IP1	SM3 PL	RoS IP1	RoS IP2	RoS PL
Cd [μg/l] (EQS_{diss}[b,c] = 0.08 μg/L)	Total	0.21	0.35	0.01	0.12	0.09	0.00	0.19	0.27	0.12	0.05	0.19	0.13	0.22	0.36	0.16	0.10	0.20
	Dissolved	0.07	0.02	0.05	0.03	0.04	0.01	0.04	0.10	0.06	0.04	0.06	0.06	0.05	0.01	0.03	0.03	0.06
	Tr. dissolved	0.05	0.02	0.04	0.02	0.03	0.01	0.04	0.09	0.06	0.03	0.05	0.05	0.04	0.01	0.03	0.03	0.06
Cr [μg/l] (EQS_{diss}[b] = 3.4 μg/L)	Total	15.0	77.1	14.8	20.1	13.2	3.08	45.1	20.8	16.2	9.18	43.4	33.6	58.1	252	13.6	9.65	46.9
	Dissolved	0.37	0.22	0.53	0.24	0.18	0.15	0.25	0.18	0.36	0.35	0.32	0.14	0.17	0.22	0.15	0.14	0.27
	Tr. dissolved	0.24	0.15	0.43	0.14	0.07	0.11	0.14	0.13	0.19	0.09	0.18	0.08	0.07	0.10	0.10	0.04	0.17
Cu [μg/l] (EQS_{bio}[b] = 0.5 μg/L)	Total	65.4	110	34.5	30.4	29.3	10.7	48.6	46.4	75.0	20.5	72.5	46.3	77.9	134	29.6	35.4	49.1
	Dissolved	17.0	14.3	19.8	8.87	11.7	3.90	14.6	11.3	16.4	8.12	21.4	11.0	26.1	6.67	3.64	8.23	7.90
	Tr. dissolved	12.1	9.29	17.8	6.34	6.56	2.26	10.2	7.52	14.5	5.66	12.8	5.56	17.6	5.25	3.35	5.45	5.98
Ni [μg/l] (EQS_{bio}[b] = 4 μg/L)	Total	12.7	39.3	9.80	11.4	8.25	1.93	14.8	11.2	11.6	6.19	21.4	18.7	27.0	99.9	9.42	6.67	26.0
	Dissolved	3.99	2.67	3.65	1.17	1.90	0.48	3.02	1.60	2.95	2.32	2.68	3.33	2.55	2.21	1.65	1.89	2.43
	Tr. dissolved	4.22	2.47	3.52	0.98	1.48	0.32	2.39	1.49	2.69	2.05	2.29	2.91	2.03	2.13	1.36	1.52	1.95
V [μg/l] (No EQS available)	Total	22.0	63.6	21.6	20.3	12.1	3.69	43.9	21.8	24.4	8.72	37.8	24.3	49.5	186	14.0	9.36	40.9
	Dissolved	0.37	0.12	5.10	0.28	0.15	0.57	0.31	a	0.32	0.21	1.08	0.80	0.84	0.85	0.24	0.23	0.59
	Tr. dissolved	0.03	a	4.70	0.30	0.16	0.63	0.15	0.09	0.15	0.02	0.28	0.10	0.30	0.26	0.17	0.14	0.48
Zn [μg/l] (EQS_{bio}[b] = 5.5 μg/L)	Total	334	384	203	194	82.1	54.3	285	189	350	79.6	282	153	302	538	212	135	198
	Dissolved	150	40.2	131	65.6	34.8	20.8	64.3	29.4	130	41.3	105	50.8	73.6	5.79	78.9	52.7	21.3
	Tr. dissolved	146	33.6	133	56.7	28.8	17.6	57.9	29.3	121	36.9	88.6	45.8	54.9	3.58	78.6	50.3	18.7

[a] Concentrations lower than blank concentrations.
[b] Swedish national environmental quality standards (EQS) (Cd and Ni) as well as nationally implemented EQS from the European water framework directive (Cr, Cu and Zn) for annual average dissolved (<0.45 μm) Cr and Cd, and annual average predicted bioavailable Cu, Ni and Zn (SwAM, 2019).
[c] EQS_{dis} for Cd for a water hardness of 1–50 mg CaCO3/L.

smallest contribution of truly dissolved V occurred in RF1 at IP2 as the EMC were below the unusually high concentration in the blank sample. Greatest contributions of truly dissolved metals (as a percentage) were found in RF1 at PL for Cd, Cu, V and Zn and in SM1 at PL for Cr and Ni. This pattern with higher percentages of truly dissolved Cd, Cu and Zn relative to total EMCs during RF events in comparison to SM events is opposite to the pattern found for particulate metal EMCs which indicates that lower concentrations in the truly dissolved fraction potentially were a function of the higher concentrations of particulate metal EMCs during SM events. However, the trend did not occur at a level that was statistically significant ($p > 0.05$). Considering that both highest and lowest percentages of all truly dissolved metals apart from V, were reported at PL could suggest that the small catchment was more susceptible to changes in land cover activities (e.g. traffic density and use of antiskid materials).

In terms of overall trends, moderate positive correlations were found between TSS and truly dissolved Cu EMCs at IP1 ($r^2 = 0.49$) and IP2 ($r^2 = 0.72$), colloidal Cu, Ni and Zn at IP1 and truly dissolved Cr at IP1. Whereas at PL, the only correlation with TSS was seen for truly dissolved V ($r^2 = 0.91$). These results could suggest that the correlation with TSS and truly dissolved metals was land use specific. However, sources of TSS were, most likely, not merely land use specific as the responsibility for winter maintenance with gritting application was shared between industries, at the industrial parks, and municipality, at PL and roads at IP1 and IP2. A rapid turnover in the industrial parks could also have resulted in temporary sources of TSS due to construction works within the industries. Even so, the correlations with TSS suggests that particulates could be a source of colloidal and truly dissolved metals, due to dissolution, whereas the lack of correlation with TSS would indicate that the sub-dissolved metal fractions originate from other, immobile sources. Such sources could be corrosion and leaching of building materials and structure surfaces, where metal roofs and facades have been pointed out to be major sources of Cd, Cu and Zn (Müller et al., 2020). Regarding particulate metal sources, brake dust, asphalt and tyre wear and roadside soil have all been shown to be sources of V and Cu in urban road dust (Mummullage et al., 2016), and these sources are likely to be dominating sources of these metals at PL which experienced a higher load of cars relative to the total runoff area compared to the industrial parks. The composition of roadside soils have not been analysed at the sites in this study but their inclusion in future studies is recommended to further explore this hypothesis.

Regarding the dissolved concentrations, results suggested that on average 32% of Cd (4–87%), 2% Cr (0.1–10%), 27% Cu (5–57%), 21% Ni (2–42%), 4% V (0.2–24) and 32% Zn (1–64%) of the total concentrations occurred in this fraction. The samples with highest and lowest EMCs in the dissolved fraction followed the same pattern described for the truly dissolved fractions, reflecting the fact that the dissolved fraction was mainly composed of the truly dissolved fraction, with <30% on average of the dissolved fraction consisting of metals in the colloidal phase (derived from data in Table 3), see Fig. 3. A pairwise comparison of all 18 colloidal and truly dissolved metal EMCs showed that the truly dissolved fractions were statistically significantly higher ($p < 0.05$) for all metals except Cr and V.

Regarding the dissolved fraction of Cr and V, 50% of EMCs reported a relatively higher concentration in the truly dissolved as opposed to the colloidal fraction. In >65% of EMCs, Cd concentrations in the truly dissolved fraction were approximately 5 times higher than colloidal Cd but on occasion were up to 80 times higher. In approximately 50% of EMCs, Cr in the truly dissolved fraction were twice that reported for the colloidal Cr fraction. The distribution of Cu exhibited considerable variations between fractions, with Cu EMCs in the truly dissolved fraction ranging from twice as high up to an order of magnitude higher than colloidal Cu. Similar to Cu, Ni and Zn concentrations in 37% of EMCs indicated a ten-fold greater value in the truly dissolved fraction compared to the their respective colloid concentrations.
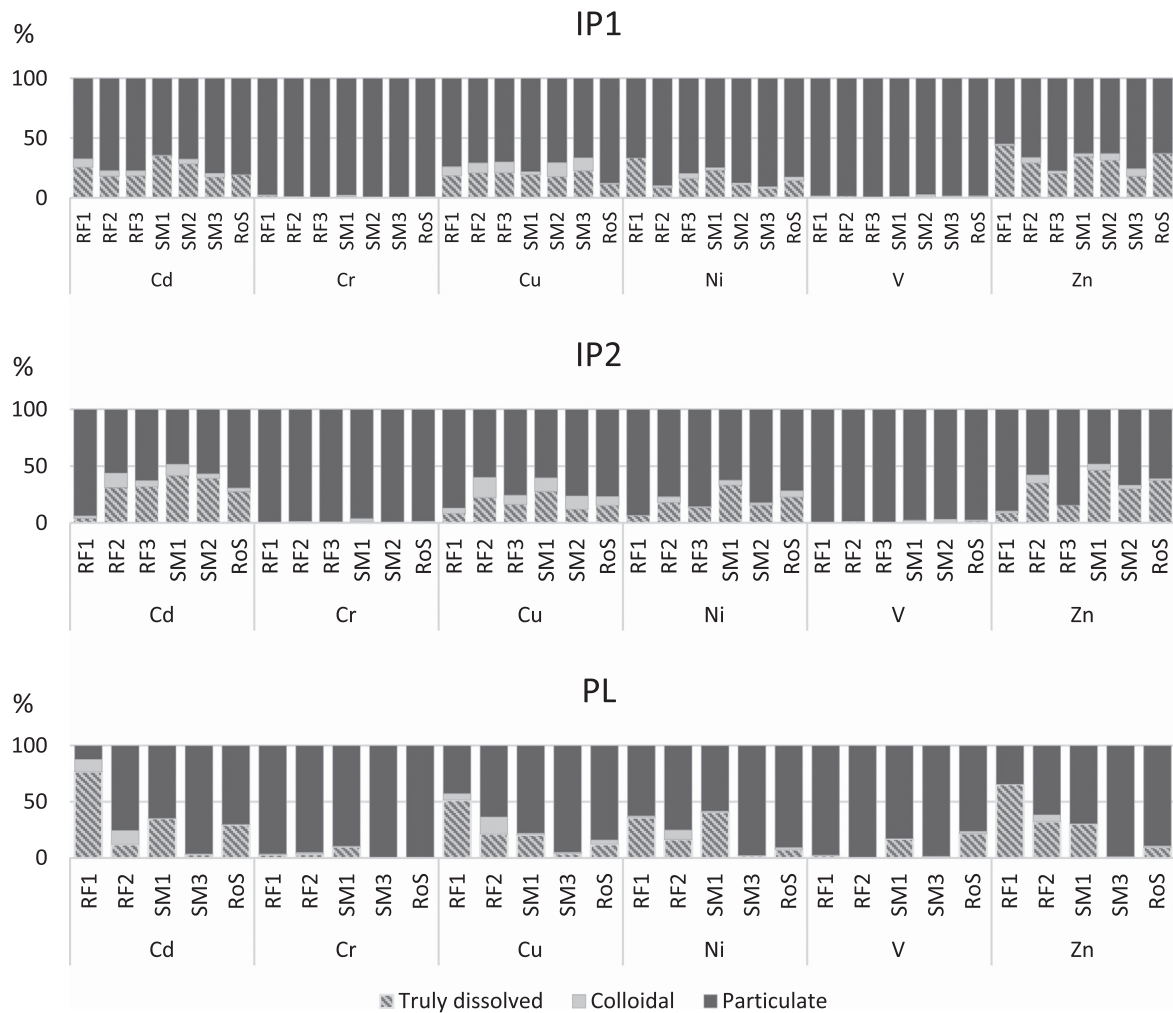
Fig. 3. Metal concentrations in the particulate, colloidal and truly dissolved fractions presented as percentage of total concentrations during 7 monitored events at the sites IP1, IP2 and PL.

Variations reported for the colloidal metal EMCs and the contribution of the colloidal fraction to total EMCs were not statistically significant ($p < 0.05$) between sites or event types. The relatively low colloidal metal EMCs reported could be a function of physicochemical processes within gully pot sediment traps, where detention can provide an opportunity for colloids to aggregate (thus contributing to suspended particulate load) and/or settle out of solution to be incorporated within basal substrates (Butler et al., 1995; Morrison et al., 1988). The variation of colloidal metal content from event to event (irrespective of event type) is not predictable and further research would be needed to enable a fuller understanding of the governing processes to be developed.

In a study by Tuccillo (2006), the colloidal metal fraction (defined as 10 kDa - 0.45 μm) was frequently reported as below the level of detection in peak flow highway and residential runoff, whereas the truly dissolved fraction (in that study defined as <10 kDa) contributed 22–100% of total Cu and 20–100% of total Zn concentrations. As reported earlier, low colloidal concentrations have been explained as a function of pavement residential time, local soil properties and a reflection of upstream sources with specific colloidal chemical signatures (Grout et al., 1999; Tuccillo, 2006). In highway peak flow runoff, McKenzie and Young (2013) reported that Cu, Cd, Ni and Zn primarily occurred in a truly dissolved fraction (<10 kDa) suggested to originate from wet deposition and transportation sector sources. The data from the current study supports both these hypothesis. However, it should be noted that the operational definition of the different fractions varied within these studies from those reported in this study, with this variation in fraction

definitions by different researchers also identified as a barrier to comparing data between studies.

3.5. Mass loads

Metal loads of the particulate, colloidal and truly dissolved fractions per unit area of impervious surface for each event at each site (referred to as "load" in the following text) were calculated and presented in Fig. 4. A pairwise comparison of loads per event between IP1 and IP2 indicated that significantly ($p < 0.05$) higher loads of Zn and V occurred at IP1 in all fractions. Particulate loads of Cd, Cr, Cu and Ni did not vary at a statistically significant level ($p > 0.05$) between the any of the catchments. However, colloidal and truly dissolved Cr, Cu and Ni displayed a significantly higher ($p < 0.05$) load at IP1 compared to IP2, as seen in Fig. 4. These results indicate that Zn and V as well as dissolved Cr, Cu, and Ni loadings originated from activities occurring more frequently at IP1 compared to IP2. For example, IP1 has more than double the annual traffic density compared to IP2. The PL, differing the most in characteristics from the other sites, only showed statistically significant differences ($p < 0.05$) in loads with IP1 for Cd in all fractions, where IP1 stood for the higher loads. Cd in runoff has been found to mainly originate from road side soil (Mummullage et al., 2016) which would explain the higher loads in IP1, with the highest percentage (25%) of green areas compared to PL (<5%). The lack of differences for other metals was understood to be a function of PL's high variability in loads between events. Calculated coefficients of variance between events for the PL were statistically significantly higher ($p < 0.05$) than for IP1 and
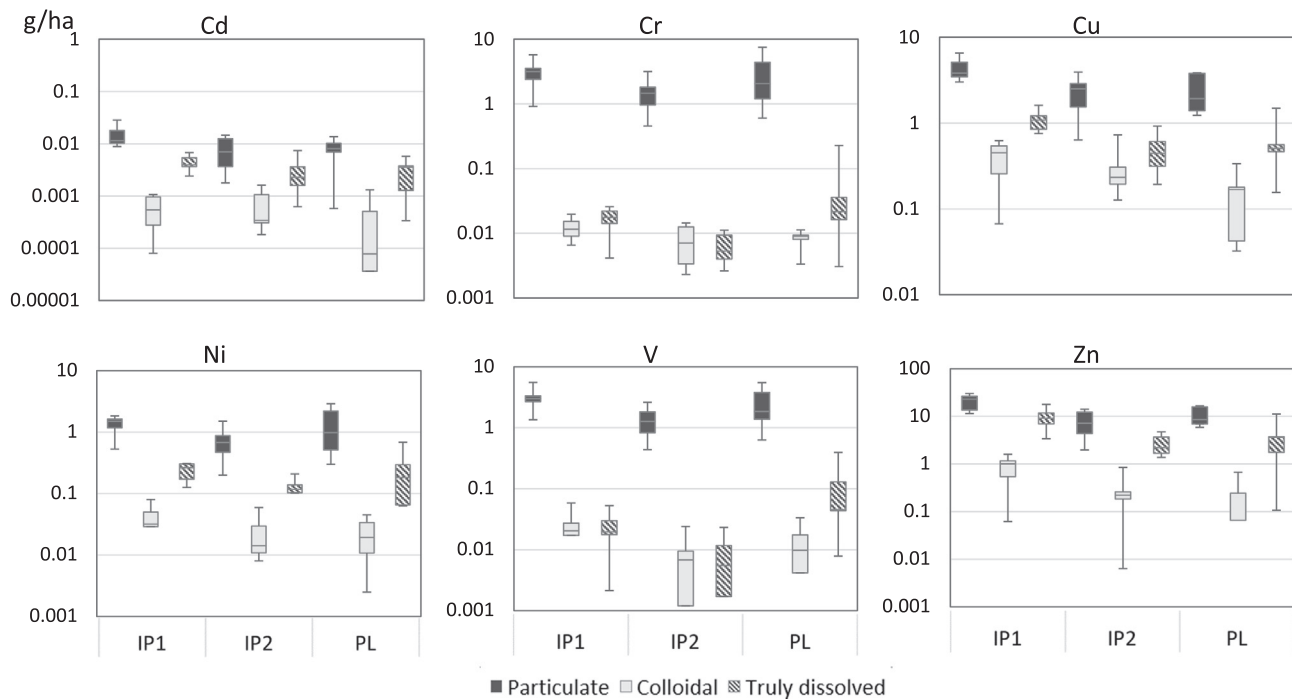
Fig. 4. Load in g/ha of impervious area for each catchment IP1, IP2 and PL of the particulate, colloidal and truly dissolved fractions. Whiskers represent the minimum and maximum loads over all events and boxes represent the 25th and 75th percentile around the median. Note the logarithmic y-axis.

IP2. This greater level of variance encompasses a range in load output at PL which overlaps that reported at both IP1 and IP2, resulting in less clear characteristic load output from PL. This greater level of variability is probably connected to the relatively higher level of imperviousness at PL resulting in a catchment that is both more flashy and sensitive to changing rainfall intensities than IP1 and IP2. The high variance between events at PL was also considered to contribute to the absence of seasonal patterns regarding loads at this site. In contrast, the particulate fraction did experience a seasonal pattern at site IP2 with higher loads during RF events compared to RoS and SM events (data not presented). This trend occurred at a statistically significant level for V ($p < 0.05$) with a slightly less strong relationship identified for Cd, Cr, Cu, Ni and Zn (significant at $p < 0.08$). The gritting event during RF3 is thought to have influenced this seasonal pattern with higher particulate loadings reported during RF events. In contrast with the particulate fraction, loads within the colloidal and truly dissolved fractions did not experience any seasonal patterns with the exception of truly dissolved Cr at IP1 and colloidal Cd at IP2 that followed the particulate fraction and showed significantly higher loads ($p < 0.05$) during RF events compared to RoS and SM events. Since the seasonal trend for particulate metals was not observed at both industrial parks the results indicate that the trend was not driven by land use type. The recorded total runoff volumes (see Table 1) at site IP1 were higher during RoS and SM events compared to RF events in relation to IP2. The relative decreasing volumes during SM could potentially be a reason why IP2 experienced this seasonal pattern and not IP1. A suggestion for the smaller snowmelt generated volumes at IP1 is that snow from a larger area at IP2 was compressed into piles compared to IP1 where the higher percentage of green areas were left undisturbed. Snow piles in designated spaces cover a smaller area than undisturbed snow distributed over larger areas and hence do not generate runoff in the same rates as undisturbed snow (Ho and Valeo, 2005).

3.6. Implications for practice

The fact that the truly dissolved fraction contributed >25% of total Cd, >18% of total Cu, 15% of total Ni and >30% of total Zn in more than 50% of samples, indicates that ultrafiltration alone would not be an efficient treatment technique with regard to removing these metals. Sweden's national implementation of the European Water Framework Directive provides environmental quality standards (EQS) of annual average concentrations for bioavailable Cu – 0.5 µg/L and Zn – 5.5 µg/L as well as dissolved (<0.45 µm) Cr – 3.4 µg/L in receiving water bodies (SwAM, 2019). Furthermore, Swedish receiving water quality guidelines considers limits for annual average effluent concentrations of bioavailable Ni – 4 µg/L and dissolved (<0.45 µm) Cd – 0.08 µg/L (SwAM, 2019). Dissolved concentrations of Cd in this study only exceeded the EQS during RF3 at IP1 (Cd EMC - 0.1 µg/L) whereas Cr did not exceed the EQS in any of the sampled events, see Table 3. Truly dissolved Cu EMCs exceeded the EQS$_{bioavailable}$ in all measured events, often by an order of magnitude (e.g. truly dissolved Cu – 5.7 µg/L in SM1 at PL) and truly dissolved Zn exceeded the EQS$_{bioavailable}$ by at least 3 times in all events with the exception of SM3 at PL. Truly dissolved Ni only exceeded the EQS$_{bioavailable}$ in one rainfall and one snowmelt event (RF1 at IP2 and SM1 at PL). The EQS$_{bioavailable}$ for metals considers modelled values based on pH, DOC and the dissolved metal concentrations and is therefore not directly comparable to the results of this study.

However, truly dissolved metals are typically considered as the fraction most available for biological uptake and their accumulation by plants as a mitigation measure has been investigated (Blecken et al., 2011; Davis et al., 2003). These studies indicated metal uptake by plants in BMPs was a relatively minor contribution to the reduction in total concentrations (Davis et al., 2009; Muthanna et al., 2007). However, if the target of treatment is the removal of truly dissolved metals, then this potential removal mechanism may need to be re-examined in light of its potential for uptake of this fraction. An alternative option could be systems that promote coagulation/flocculation processes, with a recent study (Nyström et al., 2020) reporting a 40% reduction of dissolved (<0.45 µm) Cr and Cu in urban runoff using commercially available coagulant products. In this regard, further knowledge on the differential removal performance of alternative fractions by the various treatment systems available is needed to enable treatment technologies to be selected on the basis of not only total concentrations but in relation to their potential to manage metal fractions of particular concern.

4. Conclusions

Whilst dissolved EMCs are a sum of both colloidal and truly dissolved fractions, this study shows that the truly dissolved fraction is the primary component of determined dissolved Cd, Cu, Ni and Zn EMCs, in runoff from industrial and parking lot land use. Colloidal metal concentrations contribute a relatively lower amount regardless of metal, sampling site and event type, standing for on average 16%, 42%, 28%, 13%, 10% and 44% of dissolved Cd, Cr, Cu, Ni, Zn and V respectively. The data clearly indicates that the dissolved fraction is not a homogeneous fraction and should not be treated as such. In the context of treatment, a nonhomogeneous dissolved phase is likely to require more than one approach to enable all fractions to be treated.

Distribution of the colloidal and truly dissolved fraction did not follow the patterns observed for the particulate fraction which indicate that the sub-dissolved fractions did not originate solely from dissolution and leaching from particulate matter or that release patterns per source vary by metal fraction. In terms of metal loads, outputs from PL varied greatly, reporting values both higher and lower than the loads calculated for IP1 and IP2, most probably due to PL being a highly impermeable catchment and therefore sensitive to changes in rainfall intensity. The load data revealed that all fractions of Zn and V as well as sub-dissolved fractions of Cr, Cu and Ni were higher in IP1 compared to IP2 understood to be due to the higher traffic load at site IP1. Particulate metal loads at IP2 in this study are higher during RF events compared to RoS and SM events. However, when looking at sub-dissolved fractions, neither colloidal nor truly dissolved metal loads demonstrated any similar patterns. This also supports the hypothesis that particulate matter is not the main source of truly dissolved or colloidal metals.

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CRediT authorship contribution statement

Sarah Lindfors: Conceptualization, Formal analysis, Investigation, Writing - original draft. **Heléne Österlund:** Conceptualization, Methodology, Investigation, Writing - review & editing, Supervision. **Lian Lundy:** Conceptualization, Writing - review & editing, Supervision. **Maria Viklander:** Conceptualization, Methodology, Validation, Writing - review & editing, Supervision, Funding acquisition.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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