Research article

Evaluation of measured dissolved and bio-met predicted bioavailable Cu, Ni and Zn concentrations in runoff from three urban catchments

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ABSTRACT

Urban runoff is a diffuse source of pollution contributing to the poor ecological and chemical status of surface waters. Whilst the EU Priority Hazardous Substances Directive now identifies environmental quality standards for selected metals in relation to the bioavailable metal fraction the relationship between analytically determined metal size fractions transported by urban runoff and the often variably defined concept of bioavailability has not been thoroughly evaluated. This paper provides a review of the terminology used within urban runoff studies to characterise metal fractions and behaviour. Measured dissolved and truly dissolved (determined by ultrafiltration; <3000 molecular weight cutoff) Cu, Ni, and Zn concentrations are also compared to the bioavailable metal fraction (as predicted using Bio-met, a simplified biotic ligand model) in snowmelt and rainfall derived runoff samples from three urban catchments. The study shows that predicted bioavailable concentrations were significantly lower than truly dissolved concentrations for all metals and discusses current bioavailability modelling parameters in relation to rainfall and snowmelt runoff data sets. Statistical analysis of relationships between field and predicted bioavailable data sets indicate that the bioavailable fractions originate from both colloidal and truly dissolved fractions.

1. Introduction

A review of the state of Europe's waters (EEA, 2018) reported that approximately 60% of surface waters have yet to achieve either good ecological or chemical status. Diffuse pollution is identified as affecting 38% of water bodies, over twice the number affected by point sources (18%) and on a par with pressures effected by hydromorphological changes (40% of water bodies) (EEA, 2018). Whilst agricultural activities are recognised as a major source of diffuse pollution in many river basin management plans, the contribution of pollutants deposited in urban areas and mobilised by surface runoff during rainfall and snowmelt events to receiving water loads is less certain (EEA, 2018).

The principal pollutant groups associated with urban diffuse pollution are metals, organics and nutrients coming from a mix of sources including vehicular wear and traffic emissions, roofing, construction materials, commercial activities, litter and plant/leaf debris, spillages and animal/bird excreta in addition to atmospheric deposition (Lundy et al., 2012; Müller et al., 2020). Determining the ecological impacts of this urban pollution cocktail on receiving waters is not straightforward. For example, whilst there are studies where the ecology of surface

waters downstream of urban discharge sites does not significantly differ from those upstream of the discharge point (e.g. Bruen et al., 2006), several detailed studies have reported a change in the nature or composition of downstream ecologies (Hurle et al., 2006; Kayhanian et al., 2008). However, the challenge of establishing a causal relationship between the chemical and ecological statuses remains. Whilst studies have identified metals transported in stormwater runoff as the source of toxicity in several species (Crabtree et al., 2009; Mayer et al., 2011), runoff discharges identified as exceeding metals environmental quality standards (EQS) are not consistently associated with poorer ecological status (EEA, 2018).

In terms of legislation, the EU Water Framework Directive (WFD: EC, 2000) sets out a legal requirement for Member States to protect and restore the quality of European water bodies, by establishing requirements for both good ecological and chemical status. The chemical status of surface waters is determined through the use of EQSs which, in terms of metals, were established for Cd, Ni, Pb and Hg. The EQS for metals were expressed as dissolved concentrations (defined in Annex I part B as the fraction obtained on filtration through a 0.45 μm filter) (EC, 2008) as annual average (AA) and maximum allowable concentrations

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(MAC). Monitoring of the dissolved concentrations were in recognition of the fact that metals occur in a variety of forms in aquatic systems (i.e. particulate, colloidal and free ions) and that only metals in solution (i.e. dissolved) have the potential to cross biological membranes and are therefore of greater concern (e.g. Markich et al., 2001; Wang and Guo, 2000).

A review of the EU EQS in 2011 led to the establishment of revised AA EQS for Ni and Pb which relate to the bioavailable concentration of each metal (the EU Priority Substance (PHS) Directive) (EC, 2013). This revision (a shift from dissolved concentrations to their bioavailable fraction) was in response to increased understanding of the range of parameters (i.e. pH, dissolved organic carbon, salinity and temperature) and processes (e.g. formation of metal complexes and competition for binding sites on biological receptors) which interact to determine the amount of metal that is actually bioavailable on a site by site basis (Guo et al., 2002; Smith et al., 2015). In addition to the establishment of EU EQS$_{bioavailable}$ for Ni and Pb, national EQS$_{bioavailable}$ were developed by certain Members States. For example, the UK, France and Sweden have developed national EQS$_{bioavailable}$ for Cu, Zn and Mn (Hoppe et al., 2015; SwAM, 2016; UK TAG, 2008).

In recognising the analytical challenges posed by direct measurement of the bioavailable fraction, the EU PHS Directive (2013) permits the use of 'appropriate bioavailability modelling' to take into account the influence of local water quality parameters when identifying the bioavailable concentration for purposes of compliance. To meet this need, a variety of full and simplified biotic ligand models (BLMs) have been developed and used in a range of research, risk assessment and regulatory contexts (Crémazy et al., 2017; Peters et al, 2009, 2016). In contrast to full BLMs which require input of field data on upwards of 10 parameters, simplified BLMs (such as Bio-met (2019), M-BAT (2014), PNEC-pro (2016) and Windward BLM (2019)), integrate data on dissolved metal concentrations, pH, DOC and calcium concentrations to predict the amount metal available for uptake by organisms on a site specific basis (Peters et al., 2016).

As a contribution to this field, this paper presents an overview of the terminology used to-date in characterising directly measured sub-dissolved fractions in a stormwater context and current understanding of the relationship of these fractions to the term 'bioavailable'. Field data on the dissolved and truly dissolved concentrations of Cu, Ni and Zn, pH, DOC and Ca in snowmelt and rainfall runoff derived from three urban catchments during six events is also presented. The generated data set is then used to support an evaluation of the relationship between directly measured truly dissolved concentration (as separated using <3000 molecular weight cut off; MWCO; ultrafiltration) and the predicted bioavailable metal fraction (calculated using the simplified Bio-met BLM) in relation to the validity of using truly dissolved metal concentrations as a surrogate for the bioavailable fraction.

2. Method

2.1. Study sites, sampling and analysis

Runoff from three urban catchments (two industrial parks (IP1, IP2) and a parking lot (PL)) located in Umeå, northern Sweden, was sampled from receiving stormwater pipes during three rainfall, two snowmelt and one rain-on-snow event. Site levels of imperviousness were 75%, 85% and 95% for IP1, IP2 and PL respectively, with the pervious surfaces consisting mainly of grassed areas. IP1 and IP2 were industrial 15 ha and 12 ha sites, respectively, whereas PL was a parking lot of 0.45 ha. Automatic samplers (Teledyne ISCO) were installed in storm sewer manholes on the bottom of the pipe downstream each catchment. The automatic samplers were programmed to collect volume proportional samples (a minimum of five samples and a maximum of 24 samples per event; for further details see Lindfors et al. (2020)). Samples were stored at 4 °C and transferred to the university laboratory where pH was measured and samples filtered via 0.45 μm membrane syringe filters

within 24 h of collection for analysis of metals and dissolved organic carbon (DOC). DOC samples were frozen prior to analysis. Membrane filtered samples were further processed using Sartorius ultrafiltration spin columns with a 3 MWCO for analysis of the operationally-defined truly dissolved metal concentrations. Element and DOC analysis were conducted by an accredited laboratory (ALS Scandinavia, Lulea, Sweden) where element concentrations were determined using inductively coupled plasma-sector field mass spectrometry and -optical emission spectroscopy (ICP-SFMS and ICP-OES) according to SS EN ISO 17294-2:2016 and 11885:2009. DOC concentrations were measured using oxidation and infrared-spectrometry according to DIN EN 1484 H3. All samples for DOC analysis were acidified with HCl in order to eliminate inorganic carbon such as carbonates. Control samples consisting of deionised water were included in each stage of the preparation, extraction and analysis of samples. The accreditation certifies the laboratory compliance with international QA standards, confirmed both by an initial assessment and by recurrent audits. Laboratory blanks and control materials were prepared and analysed in parallel with the samples. Concentrations of filtration blanks exceeding the reporting limits were subtracted from sample concentrations to account for any metals leaching from the filters. Statistical analysis involved Anova, t-test and linear regression. Ca, DOC and metal concentrations were not normally distributed and were log transformed before further analysis.

2.2. Event characteristics

Runoff samples were collected during a total of 15 events: three rainfall (RF-A, B and C); two snowmelt (SM-A and B) and one rain on snow (RoS) at IP1, IP2 and PL. Characteristics of the sampled events are presented in Table 1. Event durations varied from a minimum of 5 h 11 min (RF-A) up to almost 24 h (RoS). Rainfall events generally generated higher total runoff volumes than snowmelt events, with the RoS at IP1 generating the highest total runoff volume. The number of samples collected per event varied from 5 to 13 samples (see Table 1), with a total of 128 samples analysed. Baseflow samples were collected prior to

Table 1
Event characteristics of six monitored events at the sites IP1, IP2 and PL.

Dates	Event characteristics	IP1	IP2	PL
RF-A: 16/6/16 6 ADD	Duration	5 h 45 min	5 h 11 min	5 h 59 min
	Total runoff volume (m^3)	711	444	38
	Number of samples	7	6	8
RF-B: 10/10/17 2 ADD	Duration	12 h 5 min	14 h 58 min	14 h 55 min
	Total runoff volume (m^3)	2032	1521	92
	Number of samples	13	12	11
RF-C: 11/11/17 3 ADD	Duration	13 h 23 min	No	10 h 53 min
	Total runoff volume (m^3)	1453	data	168
	Number of samples	6		13
SM-A: 16/3/17 7 ADD	Duration	10 h 53 min	17 h 39 min	No
	Total runoff volume (m^3)	836	377	data
	Number of samples	7	5	
SM-B: 22/3/17 1 ADD	Duration	9 h 28 min	No	11 h 5 min
	Total runoff volume (m^3)	704	data	13
	Number of samples	7		6
RoS: 14/11/16 7 ADD	Duration	23 h 21 min	23 h 47 min	21 h 35 min
	Total runoff volume (m^3)	2577	1011	42
	Number of samples	12	9	6

Key; ADD = antecedent dry days.

every event at IP1 and IP2 (no baseflow at PL) with the exception of RoS; a total of 5 and 3 base flow samples from IP1 and IP2, respectively. For further site and event characteristics see Lindfors et al. (2020).

2.3. Bioavailability modelling using bio-met

Biotic ligand models (BLMs) are mechanistic models that combine an equilibrium geochemical speciation model, a metal–organic binding model and a toxicological model to predict the amount of metal which will occur in a bioavailable form on a site specific basis (Smith et al., 2015). However, their operational complexity (i.e. input data requirements and skills required to interpret data) together with extended runtimes has led to the development of simplified bioavailability assessment models for both establishing and monitoring compliance with $EQS_{bioavailable}$ (Hoppe et al., 2015; M-BAT, 2014). Bio-met is a simplified BLM available for free online as an output of the Bio-met initiative (a collaboration of European metals trade associations and consultancies) (Bio-met, 2019). Bio-met was developed as a rapid, low-data requirement alternative to the use of data-demanding full-scale BLMs or expensive, time consuming laboratory bioassays. Bio-met was used in this study, as opposed to other simplified BLMs, due to its use among practitioners (e.g. Umeå_kommun, 2018). The Bio-met tool integrates site specific pH, Ca and DOC concentrations data to generate metal-specific local HC5 values (i.e. the metal concentration which is hazardous for 5% of the species challenged) and predict the bioavailability of Cu, Ni, Zn and Pb. However, at the time of writing, it was not recommended to use the model for calculations of bioavailable Pb for chemical status classification under the WFD (User Guide, 2019). The local HC5 levels are obtained from full BLMs based on data generated from a range of bioassays carried out in several European countries. Under sensitive site conditions, i.e. conditions of maximised bioavailability based on the input parameters, the local HC5 would equal the reference condition (conditions of high bioavailability) i.e. the environmental quality standard for bioavailability ($EQS_{bioavailable}$). The model then introduce a BioF which represents the fraction of the dissolved metal concentration which is bioavailable. It is established as the ratio between the reference HC5, the expected bioavailability at the reference site, and the derived local HC5 and will always equal 1 or less. The bioavailable metal concentration is then calculated as the BioF times the dissolved metal concentration in µg/L. Validated operational ranges for pH, Ca and DOC inputs (see Table 2) are pre-defined for each metal through reference to the respective full-scale BLMs. Samples which fall outside the validated ranges are automatically allocated the closest value from the under-pinning BLM database.

3. Results and discussion

3.1. Sub-dissolved metals; key terms and definitions

Filtration is a common aqueous separation technique, with the use of a filter with a specific pore size resulting in a filtrate with an operationally-defined - in this case - metal fraction. For example, the use of a 0.45 µm filter is identified in Buffle et al. (1992) to distinguish between total and dissolved metal concentrations. In line with scientific and legislative developments in the field of environmental protection e. g. the revision of selected metal EQS to target the bioavailable fraction

Table 2
Ranges for pH, DOC and Ca within which the Bio-met tool is validated. Ranges has been defined for each metal based on the bio assays underlying the simplified BLM.

Parameter	Validation range Cu	Validation range Ni	Validation range Zn
pH	6.0–8.5	6.5–8.2	5.5–8.5
DOC mg/L	0.1–30	0.1–30	0.3–22.9
Ca mg/L	3.1–129	2–88	4.8–160.3

(EU PHS Directive, 2013), increasing attention has focused on the development and application of techniques to characterise sub-dissolved (i.e. <0.45 µm) metal fractions. Several studies have supplemented the traditional approach of reporting total, particulate and dissolved metal concentration with, for example, the use of ultrafiltration techniques. Ultrafiltration is a separation technique that involves the use of filters which separate substances according to their molecular weight. The technique has been used as a step in drinking water production, municipal and industrial wastewater as well as stormwater treatment (Zhang et al., 2019; Collado et al., 2020; Faragò et al., 2019; Göteborgs Stad, 2020; Ortega Sandoval et al., 2019). The most commonly used ultrafilters in previous studies on stormwater quality were in the range 3000–50,000 MWCO (often also referred to as Dalton (Da)) (e.g. Morrison and Benoit, 2005; Ortega Sandoval et al., 2019; Tuccillo, 2006). In the field of protein separation, filters in this MWCO range have been approximated to be equivalent to 2.5–6 nm pore size (Yoon, 2016).

However, in contrast to the conventional use of a 0.45 µm filter to identify metals in the dissolved fraction, the use of ultrafiltration to identify sub-dissolved metal fractions (and the associated terminology) has yet to be harmonised. This has led to the use of ultrafiltration to identify a number of differing size fractions which are then described using a range of overlapping terms (Town and Filella, 2002). Fig. 1 provides an overview of the range of operationally defined size fractions, terms used to describe these fractions and the overall relationship with changes in mobility described in a number of urban runoff studies. For example, the use of 'ultra-fractionation' techniques has resulted in the smallest fraction determined being reported as the "true" dissolved fraction (Grout et al., 1999) or, simply denoted "dissolved" (as the <0.45 µm fraction was not determined in these studies) (McKenzie and Young, 2013; Tuccillo, 2006). The colloidal metal fraction was generally derived by subtraction of the ultrafiltrate concentration from that determined in the 0.45 µm filtrate (Grout et al., 1999; McKenzie and Young, 2013; Tuccillo, 2006). McKenzie and Young (2013) further divided the colloidal fraction into light and heavy colloids by centrifugation and filtration processes and Baumann et al. (2011) denoted the size fractions after their size range (see Fig. 1). The many operational definitions used in the literature complicates comparisons between different runoff studies. One approach to clarifying this current mixed use of terminology would be for future studies to move away from the use of subjective terms (such as dissolved and truly dissolved), and instead report data using unambiguous terms (e.g. < 0.45 µm or < 3 kDa).

Key: UC – ultracentrifugation, size cut-off not determined.

As described below, the terms "truly dissolved" and "colloidal" often appear in discussions about bioavailability. As a concept, 'bioavailable' is broadly understood as 'the fraction available for uptake by organisms' (Lartigue et al., 2020). However, the term itself is used in the literature in a variety of contexts and in relation to a range of operationally defined fractions and, as such, there appears to be no clear scientific consensus on which size fractions contribute to the bioavailable concentration; a fraction of increasing regulatory importance. For example, the term bioavailable is used in relation to the freely dissolved constituents (McKenzie and Young, 2013), concentrations or activities of free metal ions (Clifford and McGeer, 2010; Smith et al., 2015; Worms and Wilkinson, 2008), labile concentrations (Pesavento et al., 2009) and the truly dissolved fraction (Brown, 2002). Further studies report that colloids can also be bioavailable (Grout et al., 1999; McKenzie and Young, 2013), with research by Guo et al. (2002) reporting that low-molecular weight colloids are 'more bioavailable' than high-molecular weight colloids. Analytical techniques available for the direct measurement of one or more of these species include ion selective electrodes (free ions), diffusive gradient in thin films (DGT) (free ions and labile species), ligand exchange cathodic stripping voltammetry (free ions and labile species) and x-ray absorption spectroscopy (bioavailable fraction) (Hayman et al., 2019; Luider et al., 2004; Pesavento et al., 2009; Ure and Davidson, 2002). However, the field concentration of these
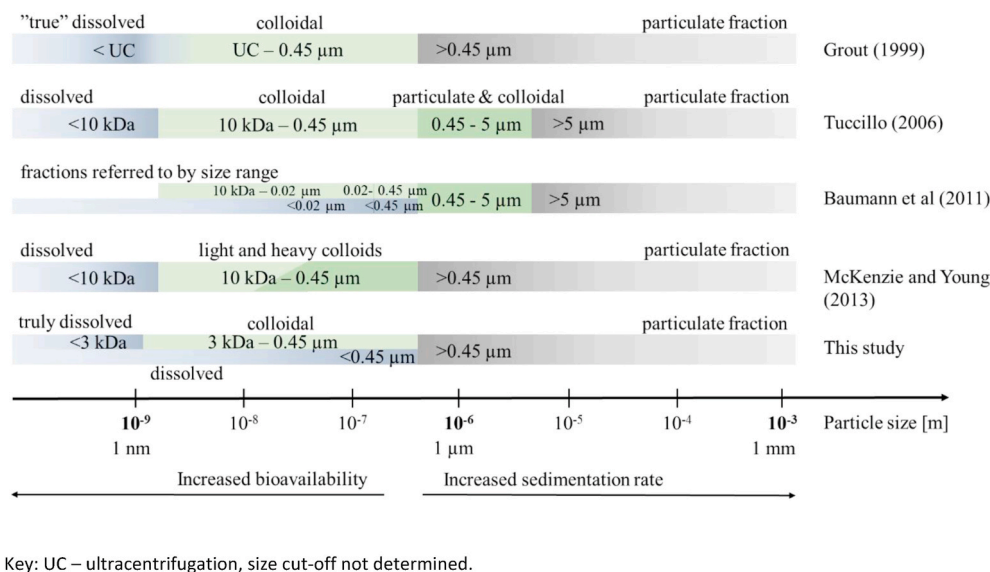
Key: UC – ultracentrifugation, size cut-off not determined.

Fig. 1. Operational definitions of size fractions and associated metal species (categories) in previous stormwater studies and current study.

sub-dissolved fractions are typically low and subject to interference, and hence results can be complex to interpret within a regulatory context (Pesavento et al., 2009). To date, ultrafiltration has been used within the field of bioavailability and toxicity research to study uptake of metals by marine bivalves (Guo et al., 2002) and aquatic moss (Öhlander et al., 2012) in the bioavailability of nanoparticles (Klaine et al., 2008) where it offers a potentially rapid approach to the separation of the truly dissolved phase for subsequent characterisation using conventional chemical analytical techniques.

3.2. Concentrations of selected metals and basic parameters determined in field samples

Measured metal concentrations in the total, dissolved and truly dissolved fractions in runoff during rainfall, snowmelt and rain on snow events are presented in Table 3 (adapted from Lindfors et al., 2020). Whilst median Cu, Ni and Zn concentrations were generally highest in snowmelt runoff in all fractions, maximum metal concentrations were determined in rainfall events (reporting wider concentration ranges than the other event types). Total metal concentrations in this study decreased in the order Zn > Cu > Ni as previously reported for urban runoff (Helmreich et al., 2010; Westerlund et al., 2003). Dissolved and truly dissolved metal concentrations also followed this order for all event types except for the dissolved and truly dissolved Zn concentrations at PL during snowmelt events (see Table 3; decreased Cu > Zn > Ni in both dissolved and truly dissolved fractions). A factor in this may be the application of salt as a de-icing agent at PL during the winter season (Na concentrations in snowmelt compared to rainfall runoff were 70 times higher at PL and about 15 times higher at the IPs, data not presented) as salts (via ion-exchange) are reported to increase metal, and especially Cu, mobility (Bäckström et al., 2004; Schuler and Relyea, 2018). Median metal concentrations in baseflow were within the overall range reported for the runoff samples, with lower maximum concentrations than the reported runoff samples.

Concentrations of Ca, DOC and pH are reported in Table 4. Values were within the range previously reported in stormwater (e.g. Galfi et al., 2016; Makepeace et al., 1995; McElmurry et al., 2014). Median DOC levels were highest in runoff samples during snowmelt events with maximum DOC values at IP1 and PL. However, median DOC levels in baseflow samples exceeded median levels in runoff reported at IP1 and IP2. Furthermore, median DOC concentrations measured in the baseflow of this study (29 mg/L and 45 mg/L at IP1 and IP2, respectively)

occasionally exceeded by an order of magnitude DOC concentrations found in groundwater globally (McDonough et al. (2020) reported 3.8 mg/L DOC concentrations on average from six continents) as well as values reported for the five northernmost counties of Sweden (1.6 mg/L DOC on average (Lundmark et al., 2015)). It should be noted that the specific compounds of organic carbon occurring was not determined (out of scope of this study). The elevated DOC concentrations in the baseflow might be due to input of organic carbon from anthropogenic sources and activities occurring at the industrial parks e.g. oil and lubricants from washing of vehicles. The Ca concentrations in the baseflow were also significantly higher ($p < 0.05$) than the levels reported in the runoff samples, indicating the inclusion of groundwater, leaching Ca from surrounding soils, to the baseflow. The site without baseflow, PL, experienced the lowest and highest event median Ca concentrations in rainfall and snowmelt runoff, respectively, possibly due to application of grit and salt during the cold season as winter maintenance. Ca concentrations in runoff showed similar levels of variations to that identified for both DOC and metal concentrations whereas pH varied little between the event types and baseflow.

3.3. Prediction of bioavailable concentrations using the bioavailability model bio-met

Of the 128 samples, pH and Ca levels were below the metal-specific validated ranges in 21 and 38 samples, respectively (see Table A in supplementary material). In these circumstances, model guidelines recommend using the closest validated value as a surrogate for the 'out of range' value. In three samples for each metal (recorded within different events) DOC levels were above the validated range (see Table 2). pH fell below the validated range for Ni in all samples at IP2 and PL during RF1 and for two samples at IP2 during RoS. Considering that pH levels below 6.5, which is the lower limit for calculating bioavailable Ni, are not exceptional in urban runoff samples (e.g. pH values of 4.0, 5.1 and 6.4 have been reported in rainfall and snowmelt runoff studies (Göbel et al., 2007; Tuccillo, 2006; Yuan et al., 2018)) the validated pH range for Ni could cause limitations for Bio-met in an urban runoff context. While a surrogate, validated, value can be used, the predicted bioavailability may underestimate field levels of bioavailability as the increasing dissolution of metals in lower pH environments would not be accounted for. In terms of site, samples collected from PL most often fell below the validated range of Ca for all metals. The sewer systems at IP1 and IP2 both experienced groundwater infiltration

Table 3

Concentrations of total, dissolved (Dis.) and truly dissolved (TD) Cu, Ni and Zn measured in baseflow and runoff samples from the study sites IP1, IP2 and PL during rainfall, snowmelt and rain-on-snow events.

Event type	Fraction and metal	IP1	IP2	PL
Rainfall (RF: A-C)	Total Cu µg/L	37.4 (19.9–218)	34.3 (12.8–283)	24.8 (6.09–225)
	Dis. Cu µg/L	14.5 (2.76–36.8)	10.5 (2.08–39.0)	6.27 (1.61–33.6)
	TD Cu µg/L	8.81 (1.50–27.3)	6.22 (0.01–26.3)	3.86 (0.61–31.92)
	Total Ni µg/L	11.4 (3.43–42.1)	8.88 (3.61–130)	6.29 (0.97–122)
	Dis. Ni µg/L	1.86 (0.49–10.2)	2.08 (1.10–5.55)	0.90 (0.20–6.84)
	TD Ni µg/L	1.52 (0.38–10.2)	1.86 (0.72–4.73)	0.61 (0.06–6.23)
	Total Zn µg/L	202 (98.1–1010)	79.0 (35.1–1040)	114 (27.4–1430)
	Dis. Zn µg/L	84.0 (21.5–258)	38.0 (10.5–79.4)	15.8 (7.14–249)
	TD Zn µg/L	74.8 (18.5–270)	30.7 (3.84–65.2)	13.6 (4.71–262)
Snowmelt (SM: A-B)	Total Cu µg/L	76.7 (57.6–132)	52.8 (24.5–71.2)	128 (56.4–294)
	Dis. Cu µg/L	23.7 (15.8–42.8)	11.4 (7.57–12.4)	6.79 (4.65–7.59)
	TD Cu µg/L	14.3 (8.73–32.7)	5.4 (4.52–7.11)	4.94 (3.13–15.1)
	Total Ni µg/L	25.5 (13.1–36.2)	20.3 (8.1–31.5)	92.9 (39.5–225)
	Dis. Ni µg/L	2.55 (1.97–5.08)	3.38 (2.75–4.62)	2.28 (1.71–2.45)
	TD Ni µg/L	2.13 (1.66–4.60)	2.65 (2.59–3.75)	1.99 (1.58–2.57)
	Total Zn µg/L	292 (216–542)	169 (92.5–219)	487 (223–1220)
	Dis. Zn µg/L	93.3 (50.9–173)	47.2 (39.2–73.5)	5.28 (3.87–7.35)
	TD Zn µg/L	84.3 (35.8–155)	43.1 (36.2–66.0)	2.59 (1.54–5.89)
Rain on snow (RoS)	Total Cu µg/L	26.1 (16.5–73.1)	33.1 (21.4–49.8)	25.1 (15.3–164)
	Dis. Cu µg/L	3.73 (2.52–5.95)	8.97 (2.28–20.5)	6.21 (4.55–19.4)
	TD Cu µg/L	3.37 (1.85–5.46)	5.98 (0.01–12.6)	4.04 (3.16–15.9)
	Total Ni µg/L	8.66 (6.26–16.7)	5.58 (2.14–9.83)	14.0 (8.32–79.9)
	Dis. Ni µg/L	1.52 (0.82–5.75)	1.87 (1.45–3.40)	1.48 (1.02–8.25)
	TD Ni µg/L	1.20 (0.64–4.71)	1.56 (1.04–2.81)	1.01 (0.52–7.73)
	Total Zn µg/L	216 (142–417)	107 (92.3–289)	96.3 (61.2–710)
	Dis. Zn µg/L	79.9 (52.1–207)	50.2 (29.7–100)	14.1 (11.0–60.5)
	TD Zn µg/L	81.3 (51.8–205)	48.5 (27.2–100)	10.8 (7.9–61.0)
Baseflow (All events excl. RoS)	Total Cu µg/L	24.4 (8.16–52.5)	20.1 (15.4–29.8)	No baseflow
	Dis. Cu µg/L	16.3 (3.95–38.6)	12.3 (7.01–17.9)	
	TD Cu µg/L	11.5 (0.50–25.6)	7.47 (6.36–11.0)	
	Total Ni µg/L	9.80 (4.26–12.3)	7.16 (4.62–10.0)	
	Dis. Ni µg/L	8.86 (3.15–10.5)	6.16 (3.56–7.08)	
	TD Ni µg/L	8.18 (2.52–9.64)	5.15 (3.00–7.02)	

Table 3 (*continued*)

Event type	Fraction and metal	IP1	IP2	PL
	Total Zn µg/L	158 (94.3–230)	49.7 (12.3–74.8)	
	Dis. Zn µg/L	99 (80.5–202)	30.0 (7.08–58.5)	
	TD Zn µg/L	84.4 (65.6–159)	22.2 (4.97–42)	

Key: data presented as median (range) concentrations.

Table 4

Concentrations of dissolved Ca and dissolved organic carbon (DOC) and pH at the sites IP1, IP2 and PL during baseflow and runoff events.

Event type	Input parameters	IP1	IP2	PL
Rainfall (RF: A-C)	Dis. Ca mg/L	8.07 (3.57–38.5)	6.18 (4.03–35.1)	3.23 (1.00–49.2)
	DOC mg/L	4.45 (2.40–29.0)	7.35 (3.20–23.0)	5.4 (1.30–40.0)
	pH	6.8 (6.4–7.00)	6.7 (6.2–7.0)	6.8 (5.8–7.7)
Snowmelt (SM: A-B)	Dis. Ca mg/L	9.78 (7.68–18.3)	7.36 (5.79–12.9)	12.0 (8.24–25.2)
	DOC mg/L	8.40 (6.00–25.0)	11.8 (9.20–14.0)	7.95 (7.00–9.00)
	pH	6.9 (6.6–7.1)	6.8 (6.7–6.8)	7.6 (7.5–7.7)
Rain on snow (RoS)	Dis. Ca mg/L	6.21 (3.89–15.2)	6.85 (3.25–8.51)	6.08 (2.99–50.2)
	DOC mg/L	5.95 (3.40–18.0)	7.90 (4.90–28.0)	5.60 (3.70–29.0)
	pH	6.6 (6.6–7.0)	6.6 (6.5–6.8)	7.1 (6.7–7.2)
Baseflow (All events)	Dis. Ca mg/L	21.0 (7.30–44.0)	11.0 (11.00–11.0)	No baseflow
	DOC mg/L	29.0 (11.4–35.2)	42.5 (9.52–49.4)	
	pH	6.70 (6.52–6.99)	6.86 (6.72–6.95)	

Key: data presented as median (range) concentrations.

whereas the sampled sewer system at PL was dry between events. This could explain the occasionally lower Ca concentrations at PL, lacking groundwater infiltration, as the Ca levels in baseflow at IP1 and IP2 were statistically higher ($p < 0.05$) compared to the runoff samples at the same sites. This supports findings of Galfi et al. (2016) which identified the role of groundwater in contributing to elevated Ca concentrations in urban runoff systems with baseflow compared to systems without baseflow. Furthermore, the stormwater pipes in IP1 and IP2 were made of concrete, while PL stormwater pipes were made of plastic, and therefore additional Ca may have been mobilised at IP1 and IP2.

Bioavailable metal concentrations (as predicted using Bio-met) are presented in Table 5. Similar to total, dissolved and truly dissolved metal concentrations, the predicted bioavailable metal concentrations showed considerable variation, especially during rainfall events. Predicted bioavailable concentrations can be compared with the surface waters EQS$_{bioavailable}$ for Ni (4 µg/L) (Priority Substances Directive, 2013) and UK national surface waters EQS$_{bioavailable}$ for Zn (10.9 µg/L) and Cu (1 µg/L) (UK TAG, 2014). The predicted bioavailable Ni did not exceed the EQS$_{bioavailable}$ on any occasion at any site, with predicted bioavailable Cu concentrations exceeding its EQS$_{bioavailable}$ in a total of 5% of samples at IP1 and PL during both rainfall and snowmelt events. In contrast, predicted bioavailable concentrations of Zn exceeded its EQS$_{bioavailable}$ in all runoff samples at IP1 for all event types, 84% of samples at IP2 and in 16% of samples at PL indicating that, of the three metals evaluated, Zn potentially posed the greatest risk to surface waters receiving runoff from industrial parks in this study. However, whilst comparison of modelled bioavailable concentrations with EQS can be useful to put the predicted concentrations in context, the EQS$_{bioavailable}$ apply to

Table 5
Predicted Cu, Ni and Zn median (range) bioavailable concentrations (Bio.) in baseflow and runoff samples collected during rainfall, snowmelt and rain-on snow events at the sites IP1, IP2 and PL.

Event type	Metal/Site	EQSbioavailable	IP1	IP2	PL
Rainfall	Bio. Cu [μg/L]	1	0.65 (0.24–**1.28**)	0.66 (0.04–**1.41**)	0.30 (0.10–**1.22**)
(RF: A-C)	Bio. Ni [μg/L]	4	0.50 (0.21–1.38)	0.41 (0.29–1.01)	0.23 (0.09–0.57)
	Bio. Zn [μg/L]	10.9	**40.0 (13.1–83.4)**	**17.1 (2.42–31.5)**	7.16 (0.54–**65.9**)
Snowmelt	Bio. Cu [μg/L]	1	0.67 (0.23–**1.29**)	0.25 (0.16–0.32)	0.16 (0.10–0.20)
(SM: A-B)	Bio. Ni [μg/L]	4	0.55 (0.25–0.67)	0.54 (0.42–0.97)	0.61 (0.42–0.72)
	Bio. Zn [μg/L]	10.9	**26.2 (13.3–42.2)**	**11.1 (9.53–23.8)**	1.27 (0.74–1.78)
Rain on snow	Bio. Cu [μg/L]	1	0.20 (0.05–0.35)	0.32 (0.12–0.69)	0.19 (0.16–0.37)
(RoS)	Bio. Ni [μg/L]	4	0.36 (0.14–0.75)	0.39 (0.26–0.55)	0.42 (0.32–0.69)
	Bio. Zn [μg/L]	10.9	**34.1 (11.5–50.8)**	**19.8 (15.6–31.8)**	5.39 (4.85–8.07)
(All events)	Bio. Cu [μg/L]	1	0.23 (0.13–0.37)	0.39 (0.17–0.46)	No baseflow
	Bio. Ni [μg/L]	4	0.72 (0.52–1.17)	1.00 (0.61–1.05)	
	Bio. Zn [μg/L]	10.9	**18.3 (11.1–66.0)**	7.94 (1.64–**16.6**)	

Key: Values in bold exceed the corresponding EQSbioavailable.

freshwater aquatic water bodies as opposed to runoff concentrations. The magnitude of dilution offered by the receiving water should be consider when discussing the implications of predicted EQS exceedance. In this study, runoff from IP1 and PL discharges into the Ume River, a major receiving water body with estimated dilution factors of 9600 and 124,000 for mean flows at IP1 and PL respectively. These levels of dilution reduce even the highest level of Zn reported (i.e. 83.4 μg/l) to a concentration below its EQS. However, runoff from IP2 discharges to the Tvärån Stream, a small waterbody with high ecological values (Umeå_kommun, 2018). Based on flow data, this smaller receiving water offers an estimated dilution factor of 400 (Umeå_kommun, 2018). Whilst Zn concentrations at this site are still unlikely to exceed relevant EQS following dilution, it does highlight that runoff discharges from comparable catchments into smaller water bodies (i.e. with dilution factors <8) would pose a risk to receiving water ecologies.

An example of such a smaller receiving water body would be a stormwater management pond. Constructed to mitigate the impacts of urban runoff, it has been shown that they also can provide habitats for wildlife as well as other ecosystems services (e.g. Bishop et al., 2000; Moore and Hunt, 2012). Studies comparing constructed and natural ponds have found that there were no significant difference in metal bioaccumulation for macroinvertebrates (Søberg et al., 2016) as well as that certain species were less abundant in stormwater ponds compared to natural ponds (Perron and Pick, 2020; Scheffers and Paszkowski, 2013). However, data collected in this study suggests that reduced levels of biodiversity might be due to their receipt of runoff containing metals in excess of the EQS together with relatively low levels of dilution. For ponds receiving runoff as the only input of water, Zn from the sites in this study would pose a risk to potential wildlife inhabiting a pond. As discussed above, the lowest level of dilution in this study was provided by the Tvärån Stream in Umeå, which receives runoff from several discharge points. The stream was subjected to an extensive sampling campaign during 2017 where levels of dissolved As and Cd (not analysed in this study) and predicted bioavailable Zn (applying Bio-Met) were found to exceed the national EQS (Umeå_kommun, 2018). Sources of these metals were suggested to be urban runoff as well as leaching of acidic, sulphate rich soils (Umeå_kommun, 2018). These results agree with the findings of this study as catchment. IP2 is part of a larger industrial area that drains to the stream with a dilution factor of only 30. If IP2 is assumed to be representative for the whole area, a dilution factor of at least 6 would be required to ensure predicted bioavailable Zn concentrations did not exceed the EQSbioavailable.

3.4. Comparison of measured and predicted concentrations

The predicted bioavailable concentration was significantly (p < 0.05) less than the analytically measured truly dissolved concentration in all events at all sites, see Fig. 2. For example, an evaluation of the number of samples in which the bioavailable fraction contributed at

least 20% of the truly dissolved fraction identified this to be the case for Zn in 88% of rainfall runoff, 89% of rain-on snow runoff and 96% of snowmelt runoff samples, for Ni in 71% of rainfall, 78% of rain-on snow and 68% of snowmelt samples and for Cu in 8% and 4% of rainfall and rain-on snow samples, respectively. Predicted Cu bioavailable concentrations did not contribute more than 20% of the truly dissolved concentrations in any snowmelt samples.

The colloidal, truly dissolved and predicted bioavailable metal fractions (as percentage of the dissolved metal concentrations from selected events representing all event types and sites) are presented together with the flow, pH and Ca and DOC concentrations in Fig. 2 (see Figure A in supplementary materials for presentation of all events). The average percentages of predicted bioavailable concentrations in relation to dissolved concentrations for Cu were 6%, 3%, and 5% in rainfall, snowmelt and rain on snow events, respectively, 41%, 27% and 40% for Zn, respectively, and 26%, 21% and 23% for Ni, respectively. In rainfall and rain on snow events the percentage of the dissolved concentration predicted to be bioavailable generally increased over event duration by, on average, 7, 21 and 41% for Cu, Ni and Zn respectively. At the end of the events the predicted bioavailable concentrations experience a drop, most likely due to groundwater infiltration and increased Ca concentrations leading to decreased predicted bioavailability. This pattern could also be seen for snowmelt events but was not as pronounced with an average increase of 2, 10 and 15% for Cu, Ni and Zn, respectively, from start to mid of the events, with predicted bioavailability decreasing from mid-event onwards.

In contrast, trends in the truly dissolved fractions (as a percent of the dissolved fraction) did not show the same behaviour. The profile of the truly dissolved fraction generally followed that of the dissolved fraction with the truly dissolved fraction contributing an average of 84% and 93% of dissolved Zn during rainfall and rain on snow events respectively, followed by Ni (79% and 78%) and Cu (62% and 70%). During snowmelt events, the truly dissolved fraction of Ni (89% of dissolved concentrations) exceeded those reported for Zn (77%) and Cu (63%). A possible explanation for this difference in patterns between the fractions may be that the truly dissolved fraction originates from dissolution of compounds in the dissolved faction whereas the predicted bioavailable fraction is a function of all the input parameters.

Both DOC and Ca concentration data indicated the presence of first flush, but for some events there was also an increase of Ca at the end of the events (see RF-B at IP1 and SM-B at IP2 in Fig. 2). This may be a function of the relatively increasing volume of baseflow to runoff volumes towards the end of the events. Whilst predicted bioavailable concentrations depends on the dissolved metal fraction, initial decreases in Ca and DOC concentrations contributed to the elevated predicted bioavailability over the duration of events. This contrasts with the results of a previous study where toxicity tests, conducted throughout runoff events, showed that the highest toxicity impacts (and therefore presumably bioavailability) were reported in samples collected during
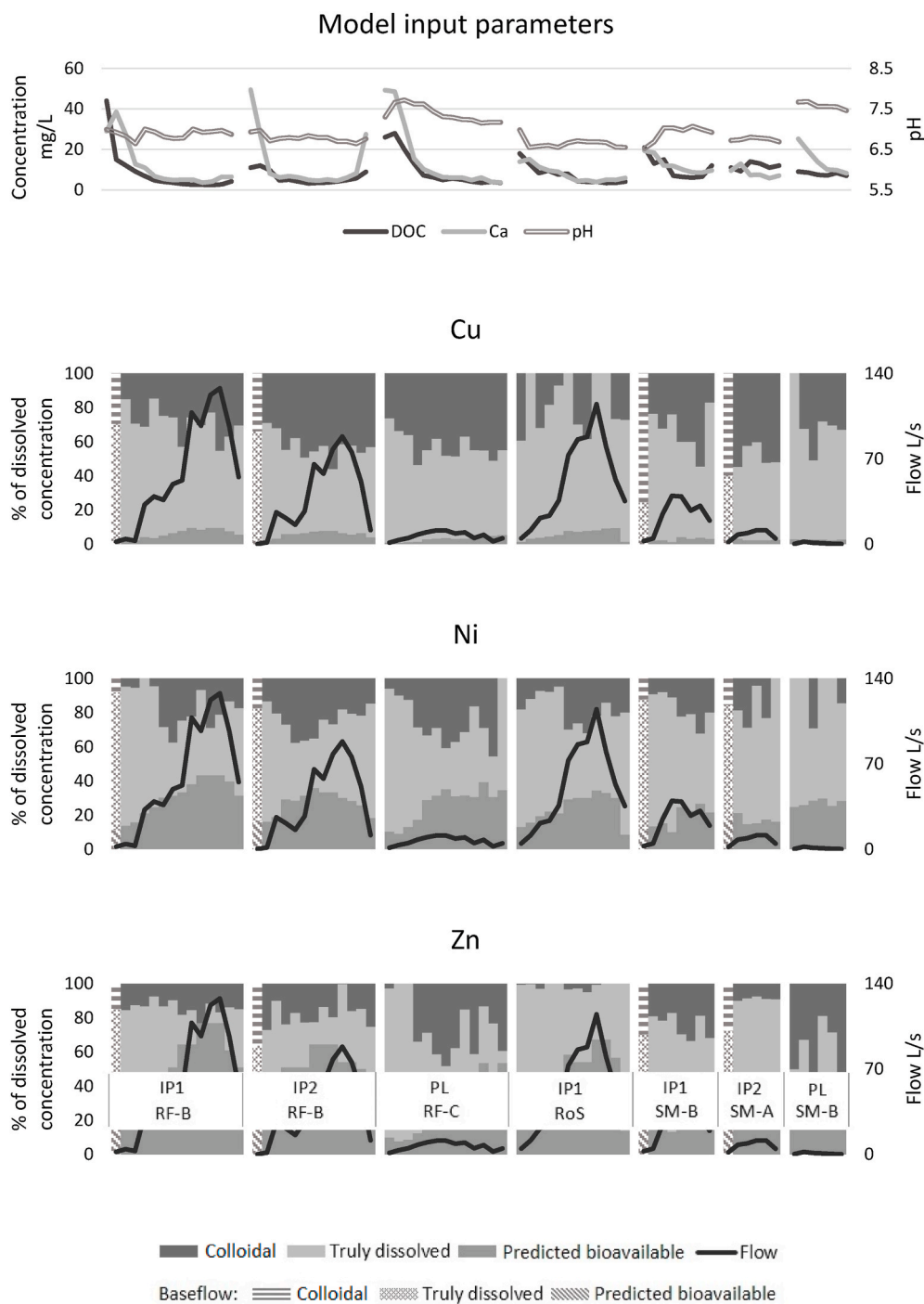
Model input parameters

Cu

Ni

Zn

Fig. 2. Profiles over the truly dissolved, colloidal and bioavailable Cu, Ni and Zn concentrations in percent of dissolved concentrations for selected events. Each bar represents a single sample.

the first flush (Kayhanian et al., 2008). The truly dissolved metal fractions on the other hand do show an indication of first flush (see Fig. 2). Since the bioavailability Bio-met model is based on tests with fixed sets of concentrations of the input parameters (i.e. data generated through static laboratory based experiments) it may not be appropriate for use within the context of the rapidly changing conditions that are characteristic urban runoff. Furthermore, the model only considers Ca as competing ion exchange element, whereas salt application during winter time would add a range of possible competing elements that would increase the bioavailability (Bäckström et al., 2004) in snowmelt events compared to rainfall events.

Despite the differences between the truly dissolved and predicted bioavailable fractions, moderate to strong linear relationships was seen between truly dissolved and predicted bioavailable Ni concentrations (R^2 values 0.47–0.96) in 11 out of the 15 analysed events. This relationship was not as strong for Cu and Zn where only 4 and 8 events, respectively, showed moderate to strong positive linear relationship (R^2 values 0.53–0.85 and 0.47–0.96, respectively; 2 events showed negative R^2 values for Cu). Further analysis also indicated positive linear relationships between bioavailable and colloidal fractions. Positive linearity was seen in 8 events for Ni and 3 events for both Cu and Zn, with R^2 > 0.47, indicating that both the truly dissolved and colloidal fraction

might contribute to the bioavailable fraction, especially for Ni. However, further research is required to test this hypothesis. To determine which size fraction, or fractions, that best reflect bioavailability, a combination of fractionation techniques in combination with parallel series of eco toxicity tests would be necessary.

4. Conclusions

This study presents measured metal concentrations in total, dissolved and truly dissolved fractions in both snowmelt and rainfall runoff as well as baseflow from three urban catchments and the sub-dissolved fractions relationship with predicted bioavailable concentrations. The results of this study suggested that:

- The predicted bioavailable concentration did not directly equate to the measured truly dissolved concentration. On average, the truly dissolved concentration exceeded the predicted bioavailable concentration by a factor of 22 for Cu, 4 for Ni and 3 for Zn. However, linear relationships with the colloidal and truly dissolved fractions indicate that both these fractions contribute to the predicted bioavailable fraction.
- National EQS$_{bioavailable}$ for Zn was exceeded by a factor of 8 in samples from one catchment. However, environmental implications depend on the dilution capacity of the receiving water.
- An initial decrease of DOC and Ca, possibly due to dilution of baseflow (which reported elevated DOC and significantly higher Ca concentrations), contributed to increasing predicted metal bioavailability over event duration.
- Differences in the predicted bioavailable fraction as opposed to measured data are potentially a consequence of bioavailability model design in that it was developed under static – as opposed to dynamic – conditions. The use of simplified BLMs within a rapidly changing water quality context is highlighted as requiring further research.
- Further research on the relationship between bioavailable concentrations (as identified using eco toxicity tests and simplified BLMs identified to assess compliance with EQS) and analytically determined metal size fractions is also recommended as a way to support river basin managers in identifying and implementing appropriate mitigation measures.

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.

Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.jenvman.2021.112263.

Credit author statement

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Writing – original draft, Heléne Österlund: Conceptualisation, Methodology, Writing – review & editing, Supervision, Lian Lundy: Conceptualisation, Methodology, Writing – review & editing, Supervision, Maria Viklander: Conceptualisation, Methodology, Validation, Writing – review & editing, Supervision, Funding acquisition.

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