Evaluation of Truly Dissolved and Bioavailable Metal Concentrations in Snowmelt and Rainfall Runoff

Evaluation des concentrations de métaux réellement dissous et biodisponibles dans les eaux de ruissellement issues de la fonte des neiges et de la pluie

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RÉSUMÉ

Les normes de qualité environnementale (NQE) énoncées dans la directive-cadre sur l'eau de l'UE, complétées par les NQE nationales, soutiennent les travaux d'évaluation des risques des métaux biodisponibles dans les environnements d'eau douce. Dans cet article, les concentrations de Cu, Ni, Pb et Zn dissous et réellement dissous (définis dans la pratique par ultrafiltration) ont été utilisées pour prévoir et évaluer la fraction de métal biodisponible (calculée avec Bio-met) dans les échantillons d'eaux de ruissellement issues de la fonte des neiges et de la pluie de deux bassins versants urbains. Les résultats montrent que les concentrations biodisponibles de Cu et de Zn dépassent les NQE biodisponibles et qu'il peut y avoir une variation de la fraction des métaux réellement dissous qui est également biodisponible, selon les métaux. Les résultats indiquent que la fraction de métal réellement dissous n'est pas un substitut approprié pour la fraction biodisponible de ces métaux.

ABSTRACT

Environment Quality Standards (EQS) stated by the EU Water Framework Directive complemented by national EQS support the work of risk assessments of bioavailable metals in freshwater environments. In this paper, dissolved and truly dissolved (operationally defined by ultrafiltration) Cu, Ni, Pb and Zn concentrations were used to predict and evaluate the bioavailable metal fraction (calculated using Bio-met) in snowmelt and rainfall runoff samples from two urban catchments. The results show that the bioavailable Cu and Zn concentrations exceed the EQS bioavailable and that there is a metal by metal variation regarding the fraction of truly dissolved metals that is also bioavailable. The results indicate that the truly dissolved metal fraction is not a suitable surrogate for the bioavailable fraction for these metals.

KEYWORDS

Bioavailable, Biotic Ligand Model, Trace metals, Truly dissolved, Urban Runoff

1   INTRODUCTION

The establishment of Environment Quality Standards (EQS; chemical concentrations below which adverse impacts are not expected within inland and coastal waters) are a key measure supporting delivery of the EU Water Framework Directive (EC, 2000). With regard to metals, EQS are available for Cd, Hg, Ni and Pb. This is complimented by the development of national EQS by certain Members States; for example, the UK has developed national EQS for Cu, Zn and Mn. In contrast to the majority of EQS identified in the EQS Directive (2008), the EQS for metals were established for dissolved concentrations, on the basis that only metals in the dissolved fraction are available for active uptake. Following further research (e.g. Gandhi et al., 2010), selected EQS were revised as part of the Priority Substances Directive (2013) which promotes the use of bioavailability modelling to take into account the influence of dissolved organic carbon (DOC), pH and water hardness to better estimate the fraction of the dissolved concentration which is bioavailable in practice. Experience with these models led to development of bioavailable standards for Pb and Ni. However, EQS for Cu and Zn have also been developed and are included in bioavailability models (e.g. Bio-met, M-BAT and PNEC proV6). Ultrafiltration is a technique, used to operationally define the truly dissolved fraction that occasionally is referred to as the most bioavailable fraction (e.g. Gagnon et al., 2014 and Tusseau-Vuillemin et al., 2007). This paper presents field data on the dissolved and truly dissolved concentrations of selected metals, pH , DOC and Ca in snowmelt and rainfall runoff derived from two urban catchments. Data is used to support an evaluation of the contribution of the bioavailable metal fraction (calculated using Bio-met) to truly dissolved concentrations, and conclusions drawn on the legitimacy of using truly dissolved metal concentrations as a surrogate for the bioavailable fraction.

2   METHOD

2.1   Study sites, sampling and analysis

Runoff from two urban catchments (an industrial area and a car park) that discharge to the Ume River, northern Sweden, was sampled during three rainfall and two snowmelt events. Both the industrial area (catchment area of 15ha) and the car park (catchment area of 0.45 ha) were equipped with ISCO automatic samplers located at the outlet of the respective catchment drainage systems. Automatic samplers collected flow-volume proportional samples (a minimum of five samples and a maximum of 24 samples per event). Sample tubing was rinsed with runoff water before the collection of each sample (in 1 litre plastic bottles). Samples were stored at 4^0C and transferred to the laboratory for analysis. pH was measured and samples filtered via 0.45 μm membrane syringe filters within 24 hours of collection for analysis of metals and DOC. Filtrates were subjected to ultrafiltration spin columns with a 3000 molecular weight cut off (3 kMWCO) for analysis of the operationally-defined truly dissolved metal concentrations. Element concentrations were determined using inductively coupled plasma- sector field mass spectrometry and -atomic emission spectroscopy (ICP-SFMS and ICP-AES) according to SS EN ISO 17294-2:2016 and 11885:2009, DOC was measured using the method set out in DIN EN 1484 H3. Control samples consisting of deionised water were included in each stage of the preparation, extraction and analysis of samples.

2.2   Bioavailability modelling using Bio-met

Bio-met is an on-line freely-available simplified Biotic Ligand Model (BLM) collaboratively developed by the Bio-MT initiative (a collaboration of European metals trade associations and consultancies. Bio-met is used by practitioners and EU and national environmental protection authorities undertaking risk assessments of metals in freshwater environments. Bio-met integrates site specific information on dissolved Zn, Pb, Cu and Ni concentrations, pH, Ca and DOC concentrations to predict the fraction of the dissolved metal which is bioavailable. Operational ranges for Ca and pH inputs are pre-defined for each metal and the output is presented as the bioavailable concentration (μg/l) which can be compared with the EQS$_{bioavailable}$ for Ni (4μg/l) and Pb (1.2μg/l) (Priority Substances Directive, 2013) and UK national EQS$_{bioavailable}$ for Zn (10.9μg;l) and Cu (1μg/l) (UK TAG, 2014). Samples which fall out-with the identified operational ranges are automatically allocated a default value from the under-pinning BLM database.

3   RESULTS AND DISCUSSION

A summary of site mean pH, Ca and DOC concentrations is presented in Table 1. Mean DOC and Ca concentrations show little variation between rainfall and snowmelt events at either site. However, as evidenced by the greater standard deviations, values show greater variation and higher maximum values in rainfall runoff. With regard to dissolved metal concentrations, >60% of metals occur in the operationally-defined truly dissolved fraction in both rainfall (82%, 74% and 61% for Zn, Ni and Cu,

respectively) and snowmelt (73% for Zn, 86% for Ni and 64% for Cu) events. In contrast, the mean fraction of truly dissolved Pb in the dissolved fraction is considerably lower (17% for rainfall and 9% for snowmelt events) with this understood to be a function of its greater association with the particulate phase.

Table 1. Site mean pH, Ca and dissolved organic carbon (DOC) concentrations in runoff samples collected during rainfall and snowmelt events in two differing catchments

Event type	Site	Parameter	pH	DOC (mg/l)	Ca (mg/l)
Rainfall runoff (3 events at each site)	Industrial (n=28)	Mean concentration ± SD	6.8 ± 0.2	10.1± 9.7	14.0 ± 11.2
		Range	6.4 – 7.0	2.4 - 44.0	3.6 – 38.5
	Car park (n=31)	Mean concentration ±SD	6.9 ± 0.5	9.4 ± 9.5	7.9 ± 12.3
		Range	5.8 - 7.7	1.3 - 40.0	1.0 - 49.2
Snowmelt runoff (2 events at industrial site and 1 event at car park)	Industrial (n = 16)	Mean concentration ± SD	6.9 ± 0.2	11.1 ± 5.6	11.2 ± 3.4
		Range	6.5-7.1	6.0 - 25.0	7.7 - 19.3
	Car park (n=6)	Mean concentration ± SD	7.6 ± 0.1	7.9 ± 0.8	14.4 ± 6.1
		Range	7.5 - 7.7	7.0-9.0	8.2 - 25.2

Site mean truly dissolved metal concentrations and bioavailable concentrations (as predicted using Bio-met) are presented in Table 2. The site mean concentrations for both fractions show considerable variation (as evidenced by the magnitude of associated standard deviations). This appears to be particularly apparent within rainfall samples. A possible factor contributing to this greater level of variation is that rainfall runoff samples were collected during three separate events, each of which involved sample collection over the course of the event with changes in metal concentrations recorded driven by changes in rainfall runoff intensity (data not presented). With the exception of Pb, the bioavailable fraction does not equate to the truly dissolved fraction in any samples during either event type at either site. The percentage of the truly dissolved consisting of bioavailable metals also varies on a metal by metal basis. For example, an evaluation of the number of samples in which the bioavailable fraction is at least 20% of the truly dissolved fraction identified this to be the case for Zn in 70% of rainfall runoff and 90% of snowmelt samples, for Ni in 60% of rainfall and 75% of snowmelt samples and for Cu in 13% of rainfall samples and not the case for Cu in any of the snowmelt samples. The remaining fraction for all metals within the truly dissolved concentration that is not considered bioavailable, is suggested to be associated to colloids smaller than the delimitation of 3 kMWCO of the ultrafilters. This would indicate a higher complexation grade with these colloids for Cu compared to Ni and Zn. As noted earlier, the amount of Pb determined in the truly dissolved phase is considerably lower than for the other metals (and in several samples was below the limit of detection). Data presented in Table 2 indicates that any Pb that does occur in the truly dissolved phase is primarily bioavailable. However, it should be noted that site mean bioavailable concentrations predicted are approximately two orders of magnitudes below the Pb EQS$_{bioavailable}$ (1.2 µg/l).

Table 2. Cu, Zn, Ni and Pb site mean truly dissolved concentrations (µg/l) and bioavailable concentrations (µg/l) in runoff samples collected during three rain events and two snowmelt events in an industrial area

Metal	Fraction (µg/l)	Industrial site		Car park	
		Rain event (n = 28)	Snowmelt (n = 16)	Rain event (n = 31)	Snowmelt (n = 6)
Cu	Truly dissolved	11.9 ± 7.5	14.6 ± 8.4	5.9 ± 6.3	6.1 ± 4.1
	Bioavailable	0.8 ± 0.4	0.6 ± 0.3	0.4 ± 0.2	0.2 ± 0.0
Ni	Truly dissolved	3.6 ± 3.3	2.5 ± 0.8	1.3 ± 1.4	2.1 ± 0.4
	Bioavailable	0.7 ± 0.4	0.6 ± 0.1	0.3 ± 0.1	0.6 ± 0.1
Zn	Truly dissolved	98.1 ± 63.0	82.9 ± 32.6	29.0 ± 46.3	3.3 ± 1.7
	Bioavailable	39.6 ± 23.0	30.9 ± 14.0	9.2 ± 9.4	1.0 ± 0.4
Pb*	Truly dissolved	0.02 ± 0.03	0.02 ± 0.04	0.01 ± 0.02	Not detected
	Bioavailable	0.02 ± 0.01	0.01 ± 0.00	0.01 ± 0.01	Not detected

Key: *=n above detection limit for Pb: n=16   n=7   n=13

At the industrial site, predicted bioavailable concentrations of Ni and Pb do not exceed the EQS$_{bioavailable}$ of 4 µg/l and 1.2 µg/l, respectively, on any occasion, with bioavailable Cu concentrations exceeding its EQS$_{bioavailable}$ (4 µg/l) in both event types in 15% of samples. In contrast, bioavailable concentrations of Zn exceed its EQS$_{bioavailable}$ (10.9 µg/l) in all rainfall runoff samples and 90% of snowmelt samples at the industrial site, indicating that Zn poses the greatest risk to surfaces waters receiving runoff from this site. At the car park site, bioavailable Cu concentrations do not exceed the EQS$_{bioavailable}$ during any of the monitored rainfall events with a small number of samples (7%) exceeding the standard in snowmelt events. In contrast, 22% of samples exceed the Zn EQS$_{bioavailable}$ in rainfall runoff but all Zn bioavailable snowmelt concentrations are below this value. This is probably due to dissolved Zn concentrations being five times higher in rainfall runoff at the car park compared to concentrations in snowmelt, indicating

seasonal variations of Zn speciation. However, whilst it is useful to compare predicted bioavailable concentrations with EQS to put identified concentrations in context, EQS apply to freshwater aquatic environments. The implication of runoff exceeding a specific EQS should then take into account the magnitude of the receiving water in terms of the level of dilution offered. Within the current study, runoff from both sites discharges into a major receiving water body (i.e. estimated dilution ration of 14000 and 200 000 for industrial site and car park respectively) indicating a small risk posed by the studied catchments alone. Greatest exceedance of $EQS_{bioavailable}$ was reported for Zn (which at its maximum exceeded its standard by a factor 10). Whilst the level of dilution offered by the receiving water at this site is such that Zn – following dilution – the $EQS_{bioavailable}$ is unlikely to be exceeded, stormwater discharges from similar catchments into smaller water courses may pose a risk to receiving water ecologies if the dilution factor is likely to be <10.

4 CONCLUSIONS

This study reports on measurements of the dissolved and truly dissolved metal concentrations from two urban catchments and the relationship between the analysed truly dissolved concentration and calculated bioavailable fractions in both snowmelt and rainfall runoff. The data suggests that the truly dissolved concentrations are an overestimation of the bioavailable concentrations and should therefore not be used as surrogate. The amount of the truly dissolved which is bioavailable varies on a metal by metal basis and by site, with greatest concern associated with Zn (exceedance of $EQS_{bioavailable}$ by a factor ten on occasion). Future work will include an evaluation of fractionation factors and correlation with the bioavailable concentrations as well as the presence of metals occurring as colloids in rainfall and snowmelt runoff.

ACKNOWLEDGEMENTS

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