Size fractionation of dissolved metals in stormwater in Umeå, Sweden

Fractionnement granulométrique de métaux dissous dans les eaux pluviales à Umeå, Suède

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RÉSUMÉ

C'est sous leur forme dissoute que les métaux sont généralement considérés comme les plus mobiles, toxiques et biodisponibles. Cependant, la répartition entre phase dissoute et phase particulaire est conventionnellement définie par la fraction traversant une membrane de 0.45 µm, bien qu'il soit largement reconnu que cette fraction contient également différents types de colloïdes organiques et inorganiques. Des fractionnements plus poussés de la spéciation des métaux peuvent être menés à l'aide de différentes techniques. Les connaissances concernant le fractionnement des métaux dans les eaux de pluie sont utiles pour l'évaluation de la biodisponibilité des métaux. Elles sont également utiles pour l'estimation des performances des systèmes de traitement des eaux de pluie. Dans cette étude, le fractionnement granulométrique de métaux contenus dans les eaux pluviales de quatre zones de la ville d'Umeå en Suède, est déterminé en utilisant l'ultrafiltration. L'objectif est de trouver une tendance pour la spéciation de différents métaux dans les eaux de pluie et, de cette manière, estimer la biodisponibilité de ces métaux. Les zones de captage étudiées incluent un parking, une portion d'autoroute et deux sites industriels. La campagne d'échantillonnage aura lieu au printemps 2016, les échantillons seront prélevés dans les systèmes de drainage à l'aide d'échantillonneurs automatiques.

ABSTRACT

Dissolved metals are generally considered the most mobile, toxic and bioavailable form of metals. However, the partition between dissolved and particulate phases is conventionally defined by the fraction passing through a 0.45 µm membrane, even though it is widely known that this fraction also includes different types of organic and inorganic colloids. Further size fractionation of metals in the dissolved phase can be performed using different techniques. The knowledge on the metal fractionation in stormwater is useful for assessments of the metals' bioavailability as well as the performance of stormwater treatment systems. In this study, the size fractionation of dissolved metals in stormwater from four different urban areas in the city of Umeå, Sweden, is determined using ultrafiltration. The objective is to find a pattern for the size fractionation of different metals in the dissolved phase in stormwater and, by this, estimate the bioavailability of the metals. The investigated catchment areas include a parking space, a highway and two different commercial sites. The sampling campaigns will take place in the spring of 2016, taking samples from the stormwater drainage system using automatic samplers.

KEYWORDS

Stormwater pollution, Metal fractionation, Colloids, Ultrafiltration

1 INTRODUCTION

As metals are ubiquitously present in both natural and urban environments and also pose a potential ecotoxicological threat to the environment, their occurrence in stormwater has significant research interest. The mobility and toxicity of metals are associated to the speciation of the metal (Stumm & Morgan, 1996). Truly dissolved phases are generally considered the most bioavailable and toxic form (Buffle et al., 1992). Studying this fraction is therefore of high importance in order to be able to assess the bioavailability of the metals.

Conventionally, the partition between dissolved and particulate fractions is operationally defined by filtration through a 0.45 µm membrane. Still, it is widely known that the dissolved fraction also will include colloidal phase metals. Colloids do not act as other particulate fractions concerning settling and will hence be transported similar to the dissolved phase in water (Luan & Vadas, 2015). However, the transportation of colloids is not usually hindered by processes such as precipitation or sorption in the same way as for dissolved metals. More recent research has therefore started to evaluate more size ranges of metals in surface runoff, including a “truly” dissolved fraction, defined by e.g. Tuccillo (2006) and McKenzie & Young (2013) as the fraction passing through a 10 kDa ultrafilter (ca. 0.003 µm according to Tuccillo (2006)) and by Morrison and Benoit (2005) as the fraction < 3,000 molecular weight cut off (MWCO).

Previous research has found that different metals are prone to interact with different types of colloids or particles, or remain in their dissolved form. Tuccillo (2006) performed a study on metal fractionation in urban runoff and found that both Cu and Zn were mainly either associated with particles > 5 µm or in the truly dissolved phase. Pb and Cr were in that study present completely in the > 5 µm range. The lead fractionation is confirmed by McKenzie & Young (2013), who also reported that Pb was predominantly associated with large, dense particles, while Cu and Zn were mainly dissolved. However, they also state that both Cu and Zn are found to be present in colloidal fractions, which is in contrast to the results from Tuccillo (2006). Another study by Morrison & Benoit (2005) also supports that Cu speciation in urban water is controlled by complexation with colloidal and dissolved organic matter. These findings highlight the difficulties in predicting the fractionation of metals, due to varying factors in water chemistry and different storm events. According to the knowledge gained from the literature review performed within this study, research on the metal fractionation in stormwater from specific areas, before the runoff reaches the receiving waters, has yet not been conducted.

The objective of this study is to determine the fractionation of dissolved metals in stormwater in four different catchment areas in Umeå, Sweden, including one highway, one parking space and two different commercial sites. The aim is to identify transport characteristics of metals in the dissolved phase in stormwater over the duration of a runoff event.

2 METHODS

2.1 Study sites

Four different catchment areas in the city of Umeå are considered in this study, including two commercial areas of different sizes, one parking space and one highly trafficked road. Study site A is a commercial area of about 22 ha. Site B is also a commercial area of about 12 ha. On site A, oil separators are connected to the stormwater sewers to a larger extent than on site B. Both site A and site B has constant base flow in the stormwater sewers. Site C includes runoff from a highway through the city of Umeå with a traffic density of ca. 15,000 vehicles per 24 hours. The catchment size is 18 ha. Finally, study site D includes exclusively the surface runoff from a parking space with the area of 0.45 ha. Study sites C and D do not have base flow in the stormwater sewers between runoff or snowmelt events.

2.2 Sampling methods

The sampling campaigns will take place in the spring of 2016. The sampling is performed directly from the stormwater sewers. For this, automatic samplers (Teledyne ISCO 6712) are used. Each automatic sampler holds 24 polypropylene bottles. The samplers as well as an Area-Velocity flow meter and logger (Teledyne ISCO 2150) were installed in manholes close to the outlets or connections to adjacent catchment areas of each specific site. At sites A and B, the base flow was sampled during 24 hours and analysed prior to the sampling of storm events. The base flow is also sampled prior to each storm event, in order to determine differences between base flow and runoff. The sample frequency of each sampling occasion is flow proportional, with 5-8 samples per storm event. Hence, samples from an entire runoff event, from beginning to end, can be collected. Each sampling campaign takes place after a minimum of three adjacent dry days.

2.3 Filtration

Each bottle of the collected stormwater is treated separately in order to be able to investigate the dynamics of metal fractionation in the dissolved phase over the duration of a rain event. The unfiltered stormwater samples are divided into subsamples of which one part is analysed concerning metals in order to determine the total concentrations. The unfiltered stormwater will also be analysed concerning particle size distribution, using a laser diffraction particle size analyser (Horiba LA-960). The other subsamples are filtered through a 0.45 µm polyethersulfone (PES) membrane filter in order to determine the differences with the particulate fraction and the fraction that is commonly considered as dissolved (>0.45 µm). This is also done in order to decrease the risk of clogging the ultrafilters. After the first filtration step, the samples are further filtered using Sartorius Vivaspin 20 ultrafiltration spin columns with a molecular weight cut-off (MWCO) of 3,000 and 100,000 MWCO. After adding the filtered (0.45 µm) stormwater, the columns are centrifuged (Eppendorf Centrifuge 5804) until <1 mL of sample retentate remains. This procedure is presented schematically in Figure 1 and will result in four levels of subsamples, all of which will be analysed concerning metal concentrations. All metal analyses are performed by an accredited laboratory.

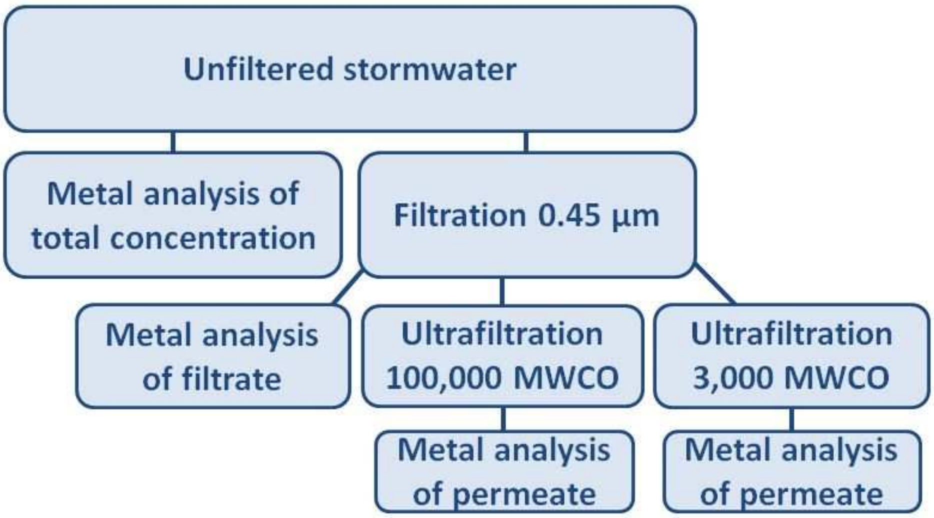

Figure 1: Filtering and analysis procedures.

2.4 Result analysis

The raw data received from the analysis laboratory is processed in order to detect any variation in metal speciation between catchment areas, different runoff events and also over the duration of single runoff events. For the visualisation of the results, selected data is presented graphically.

3 RESULTS AND DISCUSSION

The results of this study are primarily intended to characterise the size distribution of metals in the conventionally defined dissolved phase of <0.45 µm. By this categorisation it will be possible to draw conclusions about the bioavailability and, hence, the toxicity of the metals that are present in this stormwater. As environmental conditions such as concentration of organic carbon can influence the speciation of metals in water (Karlsson et al., 2009), the results may show variations from one site to another as well as within and between rain events. Comparison of the results obtained from this study and previous studies may therefore show contradictions due to dissimilar environmental conditions at particular locations.

As different types of catchment areas are investigated in this study, the results can indicate differences in metal size fractionation due to land usage of each site. By this, it might be possible to identify point sources of certain metals or site-specific conditions affecting the metal size fractionation.

Many stormwater urban drainage systems are today based on sedimentation of particles, which consequently will not remove the dissolved phase of metals. The results obtained from this study can therefore be useful in designing stormwater treatment systems with function based on the expected metal size fractionation in stormwater. Since the study also includes a particle size distribution analysis of the stormwater, the results are similarly useful to evaluate the function of existing treatment facilities in respect to the removal of particles.

Decision makers in the field of stormwater treatment can benefit from the results obtained from this study by using the information as a basis in determining if stormwater treatment facilities are needed and, if so, what type of treatment technique that is suitable.

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