Advanced size fractionation to estimate the impact of bioretention systems on metal speciation – preliminary results

Analyse fine du fractionnement par taille pour estimer l'impact des systèmes de biorétention sur la spéciation des métaux - résultats préliminaires

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RÉSUMÉ

En raison de leurs effets toxiques potentiels sur les organismes et de leur apport anthropique accru dans les eaux pluviales des zones urbaines développées, les métaux sont des polluants qui suscitent de grandes préoccupations dans les recherches sur la biorétention. Jusqu'à présent, les études sur les systèmes de biorétention des eaux pluviales ont principalement permis de déterminer la teneur totale en métaux, et, dans certains cas, les métaux dissous par filtration grâce à des filtres 0,45 µm. La présence de métaux colloïdaux n’a pas été prise en compte, bien que les effets des colloïdes sur l’environnement diffèrent de ceux des particules et des substances dissoutes. Dans cette étude, nous avons étudié dans quelle mesure le passage par des systèmes de biorétention influait sur les proportions de fractions de Cd, Pb, Cu et Zn particulaires, colloïdales et dissoutes. Les proportions des fractions colloïdales et/ou dissoutes de Cu et Zn sont plus élevées dans l’effluent qui est passé par la biorétention. Les effets du sel varient selon les métaux. Le sel affecte le fractionnement du Zn et du Cd dans l'affluent, mais pas celui du Cu ni du Pb. Le sel affecte l'effluent Zn dans la fraction colloïdale et l'effluent Cu dans la fraction dissoute. La végétation n'a pas d'impact significatif sur la spéciation des métaux. Dans l'ensemble, le traitement des métaux des colonnes de biorétention est efficace.

ABSTRACT

Due to their potential toxic effects on organism as well as their increased anthropogenic input in stormwater in urban developed areas, metals are pollutants of major concern in bioretention research. Studies on stormwater bioretention systems have so far mainly determined total metals and in some cases dissolved metals determined by filtration through 0.45µm filters. The appearance of colloidal metals has not been regarded, although environmental effects of colloids differ from particulate and dissolved substances. In this study we investigated how proportions of particulate, colloidal and dissolved fractions of Cd, Pb, Cu and Zn are influenced by passage through bioretention systems. Ratios of colloidal and/or dissolved fractions of Cu and Zn are higher in the bioretention effluent. Effects of salt vary between metals. Zn and Cd fractionation in the influent is affected by salt while Cu and Pb fractionation in influent is not affected. Effluent Zn in the colloidal fraction and effluent Cu in the dissolved fraction are affected by salt. Vegetation has no significant impacts on metal speciation. Overall, metal treatment of bioretention columns is efficient.

KEYWORDS

bioretention, metals, salt, size fractionation, stormwater

1 INTRODUCTION

Studies on stormwater bioretention systems have so far mainly determined total metal concentrations (Davis 2007, Read et al. 2008) and in some cases dissolved metal concentrations (Søberg et al. 2017, Davis et al.2003, Hatt et al. 2007). To determine the dissolved metal concentrations usually 0.45 µm filters are used. However, metals in the <0.45µm fraction are not “truly” dissolved since this fraction includes both dissolved metals and colloidal forms (Gustafsson and Gschwend 1997, Town et al. 2002). Colloidal and dissolved metals differ in bioavailability and transportability (Gustafsson and Gschwend 1997). Information on metal speciation is important to estimate the environmental impact of metals (e.g., toxicity, Janssen et al. 2003). In addition, it may help to further understand the processes in the biofilter determining metal treatment. Thus, in this laboratory study, a further subdivision of the <0.45 µm fraction was done using 3kDa filter. The metal fraction > 0.45 µm was defined as particulate, the fraction between 0.45 µm and 3 kDa as colloid and the fraction < 3kDa as dissolved. Such size fractionation can only lead to an estimation of the metal speciation in water samples, since the size ranges of particulate, colloidal and dissolved metals overlap (Gustafsson and Gschwend 1997). However, determining size fractions is a method often applied for the estimation of metal speciation in stormwater research and thus considered as applicable for this, to our knowledge, first bioretention study distinguishing between particulate, colloid and “truly” dissolved metals. De-icing salt and vegetation have been integrated as factors.

2 METHODS

An experiment with 20 vegetated (10 columns with *Carex vesicaria* and *Spartina pectinate,* respectively) and 10 non-vegetated (soil only) bioretention columns was carried out. The columns were watered with artificial stormwater. Between July and November 2017, the columns were watered with nonchlorinated tap water. Stormwater treatment started in mid of November 2017. Artifical stormwater was prepared by adding gully pot sediment to non-clorinated tap-water. CuCl2, PbCl2, CdCl2, NiCl2, ZnCl2, KH2PO4, KNO3, NH4CL and C6H5NO2 were added to achieve pollutant target concentrations. Half of the columns were watered with stormwater with added de-icing salt, the other half without salt. Mean concentration of contaminants in stormwater are shown in Table 1. Water samples were collected in end of March 2018 from the artificial stormwater and the effluent from the columns and analysed for Cd, Pb, Cu and Zn. One part of the sample was left unprocessed, other parts were filtrated with 0.45µm and 3kDa filters. Metals were analysed using ICP-SFMS, according to standard methods SS EN ISO 17294-1,2(mod) and for EPA-method 200.7 (mod) as well as ICP-AES, according to standard methods SS EN ISO 11885 (mod) and for EPA-metod 200.7 (mod) by a Swedac-accredited laboratory. When concentrations were below the detection limit, the detection limit were used for further analyses. Removal were calculated by Removal [%] = (1-Concentration Outflow/Concentration Inflow)*100. Graphics and statistical analyses (Welch’s Test and Games-Howell Pairwise Comparisons 95% Confidence) were made with Minitab ® 17.2.1.

3 RESULTS AND DISCUSSION

A comparison of the ratios of influent metal size fractions of this study (Fig.1A) with results from earlier studies on stormwater (Tuccillo 2005, Mc Kenzie et al. 2013, Grout et al. 1999) shows that the applied artificial stormwater is representative. These studies demonstrated that metal size fractionation can be very variable and depend on catchment area, rain event and measuring time during rain event.

Comparing metal size fractions in the influent and effluent shows that bioretention systems have a significant impact on the ratio of particulate, colloidal and dissolved Cu and Zn fractions (Fig.1A). Higher amounts of Cu and Zn are associated to colloids and/or “truly” dissolved after percolating through the bioretention column. Most of the Pb is particle bound in influent and effluent (Fig. 1A).

Effects of salt vary between metals. Zn fractionation in the influent as well as Cd fractionation in the influent are affected by salt while Cu fractionation in influent and influent proportions of Pb fractions are not affected. Further effluent Zn in the colloidal fraction and effluent Cu in the dissolved fraction are affected by salt. Statistical analyses reveal no effect of vegetation on metal fraction ratios in the bioretention effluent.

Comparable studies on bioretention systems have not been carried out. Søberg et al. 2017 filtered influent and effluent samples in their column experiment with 0.45 µm filters. Cu in their <0.45 fraction increased similar to our experiment after passage through the bioretention columns. However, to generalize for bioretetion systems further research needs to be carried out.

Table 1 Characterization of bioretention column in- and outflow; TSS, Cl in mg/l, metal concentrations in µg/l; N(inflow)=3, N(Carex, Spartina, no plant)=5, for Cu salt Spartina only 4 replicates; CV=coefficient of variance, ND means that concentrations were below detection limits

			Inflow			Carex			Spartina			No plant		
			Mean	CV	ND	Mean	CV	ND	Mean	CV	ND	Mean	CV	ND
TSS	no salt		170.2	(6)	-	4.9	(27)	-	6.5	(96)	-	4.2	(72)	-
	salt		161.3	(15)	-	3.1	(39)	-	7.7	(66)	-	3.7	(68)	-
pH	no salt		7.6	(2)	-	7.7	(1)	-	7.7	(2)	-	7.6	(1)	-
	salt		7.5	(4)	-	7.5	(1)	-	7.6	(1)	-	7.5	(2)	-
Cl	no salt		12.4	(4)	-	13.4	(6)	-	12.7	(1)	-	12.6	(1)	-
	salt		2657.0	(11)	-	2604.0	(7)	-	2566.0	(11)	-	2496.0	(7)	-
Cd	no salt	total	10.5	(12)	0	0.1	(0)	5	0.1	(5)	4	0.1	(0)	5
		0.45 µm	4.3	(8)	0	0.0	(24)	0	0.0	(11)	0	0.0	(4)	0
		3 kDa	4.5	(9)	0	0.0	(26)	0	0.0	(14)	0	0.0	(7)	0
	salt	total	7.5	(3)	0	0.1	(20)	3	0.1	(10)	3	0.1	(22)	0
		0.45 µm	6.3	(4)	0	0.1	(19)	1	0.1	(0)	5	0.1	(9)	0
		3 kDa	6.0	(3)	0	0.1	(20)	2	0.1	(0)	5	0.1	(17)	0
Pb	no salt	total	61.5	(8)	0	0.5	(14)	3	0.6	(28)	2	0.6	(21)	4
		0.45 µm	4.3	(45)	0	0.1	(28)	0	0.0	(10)	0	0.0	(18)	0
		3 kDa	4.3	(45)	0	0.0	(44)	0	0.0	(52)	0	0.0	(47)	0
	salt	total	45.4	(1)	0	0.7	(22)	1	0.8	(37)	1	0.5	(11)	3
		0.45 µm	1.5	(48)	0	0.2	(4)	4	0.3	(55)	4	0.2	(0)	5
		3 kDa	0.4	(12)	0	0.2	(0)	5	0.2	(0)	5	0.2	(0)	5
Cu	no salt	total	348.0	(36)	0	5.2	(20)	0	4.3	(15)	0	4.0	(17)	0
		0.45 µm	20.5	(49)	0	3.9	(18)	0	3.3	(6)	0	3.6	(17)	0
		3 kDa	13.4	(60)	0	1.5	(11)	0	1.4	(7)	0	1.5	(15)	0
	salt	total	246.0	(29)	0	13.3	(79)	0	7.7	(17)	0	8.4	(9)	0
		0.45 µm	18.0	(48)	0	6.5	(7)	0	5.8	(13)	0	6.1	(10)	0
		3 kDa	12.6	(50)	0	2.4	(8)	0	1.8	(27)	0	2.0	(9)	0
Zn	no salt	total	766.7	(15)	0	4.5	(19)	3	4.8	(19)	1	6.4	(33)	1
		0.45 µm	198.0	(9)	0	2.7	(50)	0	3.0	(35)	0	5.4	(43)	0
		3 kDa	198.0	(9)	0	2.0	(40)	0	2.2	(26)	0	3.9	(41)	0
	salt	total	507.0	(5)	0	9.7	(63)	0	7.1	(32)	0	7.8	(25)	0
		0.45 µm	250.7	(7)	0	4.7	(19)	0	4.3	(64)	0	5.7	(31)	0
		3 kDa	239.7	(8)	0	3.6	(29)	0	3.0	(24)	1	4.6	(29)	0

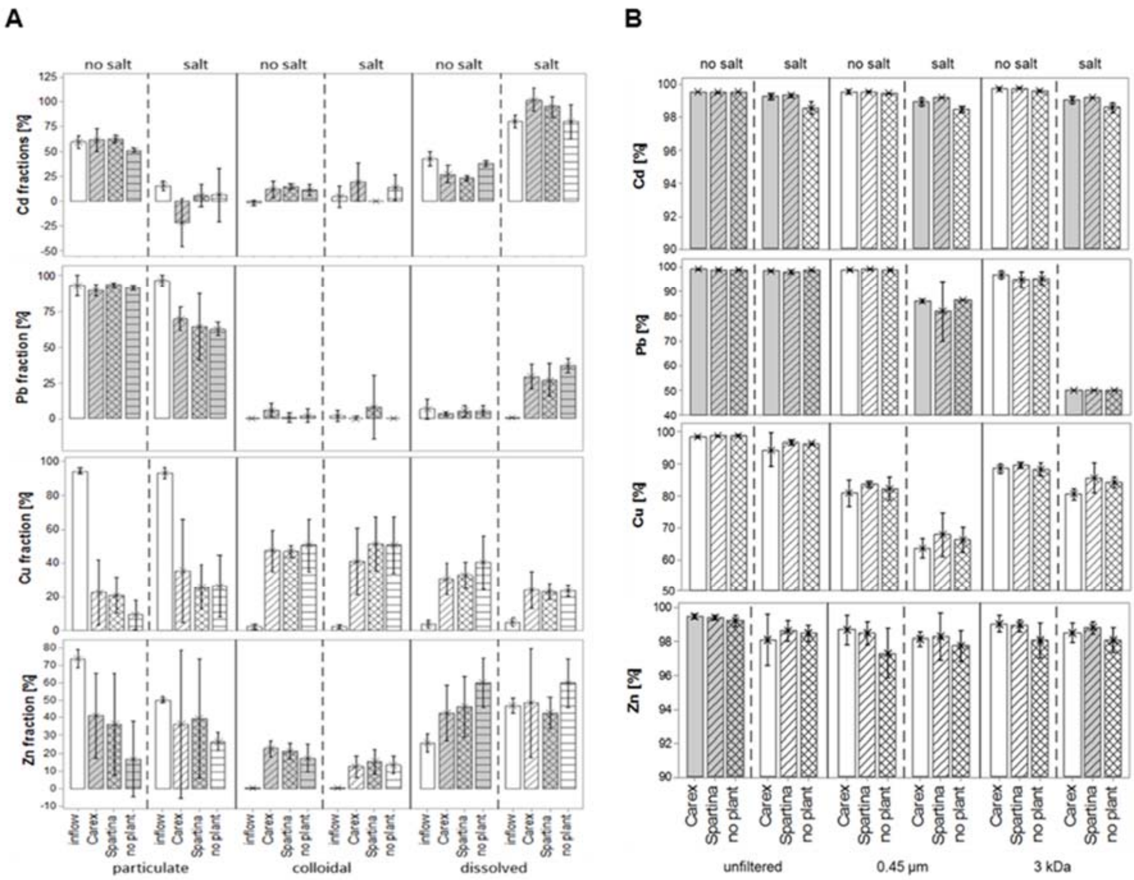

Figure 1 A Metal fractions in %, Grey bars: measurements included with concentrations < detection

limits. x = mean. Intervals calculated based on individual standard deviations; B Removal in %. Grey bars: measurements included with concentrations < detection limits. x = mean. Intervals calculated based on individual standard deviations

Overall metals was efficient treated (Table 1) with total metal removal percentages ecxceeding 95%. While influent concentrations exceeded Swedish target values for stormwater, effluent concentrations were below the values (Riktvärdesgruppen 2009; maximum reference values of Cd 0.5 µg/l, Pb 15 µg/l, Cu 40 µg/l, Zn 125µg/l). These results are in line with the commonly shown efficient total metal treatment capacities in bioretention facilities (e.g. Søberg et al. 2017, Hatt et al. 2007, Davis 2003). Salt affected overall removal of Cu significantly (Fig. 1B). Zn removal was significantly affected in unfiltered samples (Fig. 1B). The differences between salt and no salt controls in our study are not regarded to be of practical importance. For Cu, where salt showed the strongest effect on metal effluent concentration in the 0.45 µm filtered sample removal was decreased by around 15% to in average 65% (fig.1B). Significant differences between vegetated and unvegetated controls did only exist for Cd and only when salt was applied. Under these conditions, Cd removal capacities are significantly higher in vegetated controls in unfiltered and filtered samples. Even if statistically significant, no practical important effects of vegetation on removal can be detected (removal capacity decreased by <1%).

4 CONCLUSION

We could show in our study that metal fractionation is influenced by bioretention systems. However, overall metal treatment was good for particulate, colloidal and dissolved metals. Further experiments, should be carried out with adapted analyzes to overcome detection limitation. To estimate the environmental impact of bioretention systems on metal fractionation, it is particularly recommended to investigate metal fractionation on bioretention systems in the field.

LIST OF REFERENCES

Davis, A. P. 2007. *Field Performance of Bioretention: Water Quality* Environmental Engineering Science, 24(8):1048-1063

Davis, A. P., Shokouhian, M., Sharma, H., Minami, C., Winogradoff, D. 2003. Water Quality Improvement through Bioretention: Lead, Copper, and Zinc Removal Water Environment Research 75 (1): 73-82

Grout, H., Wiesner, M.R., Bottero, J.-Y. (1999). *Analysis of colloidal phases in urban stormwater runoff.* Environmental Sience and Technology. 33: 831-839

Gustafsson, Ö., Gschwend, P.M. (1997). *Aquatic colloids: Concepts, definitions, and current challenges.* Limnol. Oceanogr., 42(3):519-528

Hatt, B.E., Deletic A., Fletcher T.D. (2007). *Stormwater reuse: designing biofiltration systems for reliable treatment.* Water Science and Technology 55(4):201–209

Janssen, C.R., Heijerick, D.G., De Schamphelaere, K.A.C., Allen, H.E. (2003). *Environmental risk assesment of metals: tools for incorporating bioavailability.* 28:793-800

McKenzie, E.R., Young, T.M. (2013). *A novel approach for water constituents - distribution of storm event metals.* Environ.Sci.: Processes Impacts, 15:1006-1016

Read J., Wevill T., Fletcher T. & Deletic A. 2008. Variation among plant species in pollutant removal from stormwater in biofiltration systems. Water Research, 42(4-5), 893-902.

Riktvärdesgruppen. 2009 Förslag till riktvärden för dagvattenutsläpp. Regionplane- och trafikkontoret Stockholms Läns Landstig, Sweden

Søberg, L.C., Viklander, M., Blecken, G.-T. (2017). *Do salt and low temperature impair metal treatment in stormwater bioretention cells with or without a submerged zone?*. Science of the total environment 579: 1588-1599

Town, R.M., Montserrat, F. (2002). *Size fractionation of trace metal species in freshwater: implications for understanding their behavior and fate.* Re/Views in Environmental Science &Bio/Technology 1: 277-297

Tuccillo, M.E. (2006). *Size fractionation of metals in runoff from residential and highway storm sewers.* Science of the total Environment 355:288-300