



CHALMERS

Chalmers Publication Library

Evaluation of a passive sampler for the speciation of metals in urban runoff water

This document has been downloaded from Chalmers Publication Library (CPL). It is the author's version of a work that was accepted for publication in:

Environmental Sciences: Processes and Impacts (ISSN: 2050-7887)

Citation for the published paper:

Knutsson, J. ; Knutsson, P. ; Rauch, S. (2013) "Evaluation of a passive sampler for the speciation of metals in urban runoff water". *Environmental Sciences: Processes and Impacts*, vol. 15(12), pp. 2233-2239.

<http://dx.doi.org/10.1039/c3em00247k>

Downloaded from: <http://publications.lib.chalmers.se/publication/192510>

Notice: Changes introduced as a result of publishing processes such as copy-editing and formatting may not be reflected in this document. For a definitive version of this work, please refer to the published source. Please note that access to the published version might require a subscription.

Chalmers Publication Library (CPL) offers the possibility of retrieving research publications produced at Chalmers University of Technology. It covers all types of publications: articles, dissertations, licentiate theses, masters theses, conference papers, reports etc. Since 2006 it is the official tool for Chalmers official publication statistics. To ensure that Chalmers research results are disseminated as widely as possible, an Open Access Policy has been adopted. The CPL service is administrated and maintained by Chalmers Library.

(article starts on next page)

Environmental Monitoring and Assessment

Evaluation of a passive sampler for the speciation of metals in urban runoff water

--Manuscript Draft--

Manuscript Number:	EMAS-D-12-12651
Full Title:	Evaluation of a passive sampler for the speciation of metals in urban runoff water
Article Type:	Original Research
Keywords:	passive sampling; metal speciation; urban runoff; computer modeling
Corresponding Author:	Jesper Knutsson, graduate student Civil and environmental engineering Gothenburg, VG SWEDEN
Corresponding Author Secondary Information:	
Corresponding Author's Institution:	Civil and environmental engineering
Corresponding Author's Secondary Institution:	
First Author:	Jesper Knutsson, graduate student
First Author Secondary Information:	
Order of Authors:	Jesper Knutsson, graduate student Pavleta Knutsson, Ph.D. Sebastien Rauch, Associate professor Thomas Pettersson, Associate professor Gregory Mark Morrison, Professor
Order of Authors Secondary Information:	
Suggested Reviewers:	Johan Ingri, Professor Professor, Luleå University of Technology Johan.Ingri@ltu.se Gary Fones, Ph.D. Senior Lecturer, University of Portsmouth gary.fones@port.ac.uk Bran Vrana, PhD specialist, Masaryk University vrana@recetox.muni.cz William Davison, Professor Professor, Lancaster University w.davison@lancaster.ac.uk

Evaluation of a passive sampler for the speciation of metals in urban runoff water

Jesper Knutsson^{1†}, Pavleta Knutsson², Sebastien Rauch¹, Thomas Pettersson¹,
Gregory M. Morrison¹

5 ¹ *Water Environment Technology, Chalmers University of Technology, SE-412 96
Göteborg, Sweden*

² *Inorganic environmental Chemistry, Chalmers University of Technology, SE-412
96 Göteborg, Sweden*

10 †Corresponding author: jesper.knutsson@chalmers.se

Abstract

Metals in urban runoff water needs to be monitored in order to estimate fluxes and assess their impact on the aquatic environment. Passive sampling is a useful and reliable emerging tool for measuring time averaged concentrations of metals in water bodies. This paper describes the
15 deployment of a passive sampler to measure Cu, Ni and Zn in a storm water treatment facility. The concentrations derived from the passive samplers are compared to concentrations obtained from an automated water sampler which provides pooled spot water samples and to model predictions from the visualMINTEQ computer speciation code. Results show that visualMINTEQ predictions partly describe the metal speciation in non-equilibrium systems. Moreover, it is suggested that
20 chemodynamic models may be a suitable framework for interpretation of passive sampler results. In addition we conclude that passive samplers are a useful technique for monitoring and characterization of metal speciation in chemodynamic conditions.

Keywords: aqueous passive sampling, urban runoff, metal speciation, speciation software

25 Introduction

With the formulation of ambitious and stringent policies for the management of the quality of natural waters, such as the EU Water framework directive (WFD), new requirements have been placed on monitoring and management programs for natural waters. The WFD calls for the characterization of chemical and ecological
30 status of all major water bodies in EU member countries, as well as the mitigation of areas of concern, with the aim to reach good water status by 2015(Levy, Zhang et al. 2012). The inclusion of metals on the list of priority pollutants has also

highlighted the importance to monitor and assess the metal pollution loads in urban runoff water. A large body of work has shown that urban runoff can contain
35 high concentrations of potentially toxic metals like Cu, Cd and Ni (Florence, Morrison et al. 1992). If left untreated, urban runoff may contribute significantly to pollution from metals in recipient natural waters (Beckwith, Ellis et al. 1986; Legret and Pagotto 1999; Brown and Peake 2006; Rule, Comber et al. 2006). It is therefore desirable to be able to reliably monitor the metal fluxes in urban runoff
40 in a cost effective way. Until recently such monitoring has required technically complicated equipment and access to secure locations and infrastructures, such as electricity.

Due to the aforementioned technical and infrastructural challenges of monitoring activities, there has been an increasing interest in new and emerging technologies
45 for monitoring water quality parameters. The general perception of researchers has been that these technologies can provide additional and/or alternative measurements that can be used in the various tasks that fall within the enforcement of regulation and policy. One method for the monitoring of metals is passive sampling, which has received attention in a large number of scientific
50 publications (Zhang 2004; Warnken, Lawlor et al. 2009; Roig, Nadal et al. 2011; Tonello, Goveia et al. 2011), and also in connection with two different pan-European projects funded by the EC (i.e. STAMPS and SWIFT) (Allan, Vrana et al. 2006; Allan, Vrana et al. 2006).

The main challenge for passive sampling as a technology to be incorporated in the
55 monitoring toolbox of regulative monitoring comes from (1) formulations in policy and legislation texts, (2) lack of information about the robustness and field performance, and (3) the lack understanding of the relation between dissolved metal concentration determined by spot sampling and the fraction that is sampled by the passive sampler.

60 To address the concerns in (2) and (3) that are listed above, an investigation was carried out where passive samplers were employed in tandem with an automated water sampler in a storm water runoff sedimentation chamber. Several relevant parameters were analyzed and measured from pooled water samples and then compared with data provided by the passive samplers. In addition, a computer
65 speciation code (visualMINTEQ) was used to provide an interpretational framework for the observations.

It was shown that passive samplers can provide reliable and reproducible results when used in a variable flow regime such as the storm water treatment system. Deployment times of up to two weeks were used without significant biofouling or signs of saturation of the passive sampler. Metal concentrations derived with the passive samplers were lower than the dissolved metal concentrations measured in composite water samples. This is consistent with other studies, since the discrimination of metal species is more stringent with the passive sampler than with membrane filtration (Dos Anjos, Abate et al. ; Warnken, Lawlor et al. 2009; Tonello, Goveia et al. 2011). In addition, this study has shown the applicability of passive samplers for monitoring metal concentrations in urban storm water systems. However, a more complete understanding of the lability criteria would require the use of kinetic models rather than equilibrium models due to the governing kinetic accumulation regime of the passive sampler.

80 **Experimental**

Passive sampler

Chemcatcher, the passive sampler used in the present study (see Figure 1), comprises a watertight polypropylene body (illustrated as numbers 1,2,3 and 6), designed to hold 47 mm-diameter disks, including a diffusion limiting membrane (number 5) and an ion-exchange receiving disk (number 4) (Björklund Persson, Morrison et al. 2001; Bjoerklund Blom, Morrison et al. 2002).

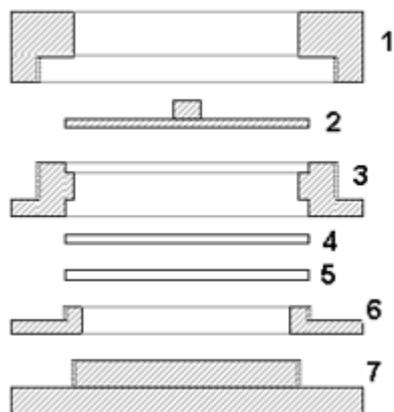


Figure 1. Exploded diagram of the passive sampler device in cross section. 1, 3, 6 sampler housing. 2. disk support. 4 Receiving 47 mm disk. 5 Diffusion limiting membrane. 7 transport lid.

90 The accumulated amount of analyte is proportional to the deployment time and to the time weighted average (TWA) concentration of the total dissolved species that

are available for the passive sampling device (i.e. device-labile) in the water. The TWA concentration can thus be calculated through

$$C_{TWA} = \frac{(M-M_0)}{R_s t} \quad (1)$$

95 where M is the mass of the analyte accumulated in the receiving phase (RP) of the sampler, M_0 is the mass of analyte in a control blank, R_s is the sampling rate given as a volume of water cleared by the sampler per unit of time, and t is the exposure time.

It has been suggested that mass accumulation of a metal present in two different species can be described by the following equation (Scally, Davison et al. 2003):

$$M = C_{ML} D_{ML} \left[1 - \exp \left(\frac{-k_{-1}(\Delta g)^2}{2D_{ML}} \right) \right] + C_M D_M \frac{At}{\Delta g} \quad (2)$$

The indexes ML and M represent metal-ligand and free metal forms respectively.

Preparation and determination of sampling rates for passive samplers

The preparation and conditioning of the Chemcatcher have been described in detail elsewhere (Runeberg 2005; Allan, Knutsson et al. 2007; Allan, Knutsson et al. 2008). The determination of sampling rates was conducted in a flow-through tank where the nominal metal concentration of the solution was kept at $10 \mu\text{g l}^{-1}$. The stock solution used for the calibration was prepared from nitrate salts of Cu, Ni and Zn respectively (>99.9% purity, Merck). Constant pH and ionic strength conditions were maintained using a NaOH-KH₂PO₄ buffer (pH 7, 0.01 mol L⁻¹ PO₄³⁻) (p.a, Sigma Aldrich) and the solution was maintained at a temperature of 18°C using a thermostat controlled heater and cooler in a water bath, in which the calibration tank were immersed.

The solution in the flow-through tank was replenished from a reservoir at a flow rate of 2 mL min⁻¹. Samples of the solution were taken daily to ensure that metal concentrations remained stable throughout the calibration. 14 passive samplers were exposed for the period of 10 days in stagnant conditions. Two passive samplers were removed from the solution daily with the exception of weekend days. The removed samplers were then extracted and prepared as described earlier. The resulting sampling rates are presented in Table 1.

Table 1. Calibrated sampling rates for stagnant conditions (0 rpm and 18 °C) single diffusion limiting membrane (Runeberg 2005).

Passive sampler R_s (ml h ⁻¹)	S.D. (ml h ⁻¹)
---	----------------------------

Cu	3.1	1.1
Ni	2.7	0.5
Zn	2.9	0.7

Field deployment of the sampler system

125 Passive samplers were deployed in a gully pot at the inflow storm water pipe
using a fixing frame arrangement. Two buoys were attached to the fixed frame
using wires, thus keeping the frame and passive samplers at a constant depth
below the water surface. The automatic water sampler was installed at the inlet
tank and was programmed to collect storm water samples in plastic bottles every
30 minutes and change sampling bottle periodically to make 6 hour pooled water
130 samples.

Six replicate samplers with were exposed simultaneously for 7 and 14 days,
respectively using a sampler holder attached to a buoy system keeping it level at
30 cm below the water surface. This assured a steady position of passive
samplers, as the water level varied by several meters in the reservoir where the
135 samplers were deployed during rain events as well as during emptying by a pump
activated through water level sensor.

An automated water sampler (6712 Full-Size Portable Sampler, Teledyne Isco)
were used to collect 50 mL water sample every 30 minutes in to a new bottle
every 6 hours. Bottles with 6 hour pooled samples retrieved every other or every
140 third day, and returned to the laboratory. The composite samples were then
divided into appropriate sub samples and prepared for analysis of several
parameters, including pH, conductivity, dissolved organic carbon (DOC), and
total and dissolved metals.

Sample preparation

145 The passive samplers were collected after exposure and the metals extracted from
the receiving disks using a vacuum filtration equipment and the addition of two 5
mL aliquots of 1M nitric acid (supra pure, Scharlau). A sub sample of the filtrate
was subsequently diluted 1:100 and 10 ppb Rh internal standard were added in
preparation for ICP-MS analysis.

150 Water samples collected by the automated water sampler were divided into four
sub-samples, and prepared accordingly for each analysis. Samples for dissolved

metals analysis were filtered through a 0.45 μm mixed cellulose ester membrane from Schleicher & Schuell, using acid rinsed glass vacuum filtration equipment. Samples were then acidified by addition of nitric acid (to make 0.14 M) and were
155 subsequently analyzed by ICP-MS. Preparation for total metal analysis was done by digesting 4 ml of the sub sample with 1 ml of nitric acid at 120 $^{\circ}\text{C}$ for 2 hours and subsequent dilution and analysis by ICP-MS.

Preparation for DOC analysis was made by filtering 50 ml of sample through a 25 mm GF/C glass fiber filter, pore size 0.7 μm , (Whatman) that had previously
160 been treated in an oven at 550 $^{\circ}\text{C}$ for 6 hours to eliminate any organic carbon residue on the filter. A glass syringe and a plastic filter holder were used to filter sample directly into brown glass bottles. The syringe and the bottles had been treated at 550 $^{\circ}\text{C}$ for 6 hours to eliminate any carbon contamination. For preservation 0.1 volume per cent nitric acid (Suprapur quality, Merck) were
165 added. Samples were then analysed using a Shimadzu TOC 5000 (repeatability 3.0%, LOQ 1.0 mg l^{-1} and LOD 0.3 mg l^{-1}).

Analytical procedures

All metal analysis was performed on a Perkin Elmer Elan 6000 ICP-MS which was tuned and optimized according to manufacturer specifications. Oxide levels
170 and doubly charged ions were at all analysis times below 3% and the background signal at m/z was below 5 cps. After optimization, the instrument gave at least 300kcps for a 10 ppb Indium solution and the relative standard deviation was better than 1%. Rhodium (10 ppb) was used as internal standard. For instrument calibration standards (0.1-500 $\mu\text{g L}^{-1}$), an ICP multi-element standard (p.a.
175 quality) from Merck (Darmstadt, Germany) was used. The reagent water used was laboratory grade I water prepared from a Milli-Q analytical water system with deionized feed water.

The DOC analysis were performed on a Shimadzu TOC 5000 instrument using TOC (total organic carbon) free (<5 ppb organic carbon) reagent water for blanks
180 and preparation of standards. LOD for this method was 0.3 mg l^{-1} .

Speciation modeling software

For software predictions of metal species availability, visualMINTEQ v 2.32 speciation software was used that is a Windows based program and a development of the MINTEQA2 speciation code, originally written in 1999 by CEAM, USEPA

185 (Gustafsson 2006). The model used in the software incorporates the NICA-
 Donnan model for equilibrium-speciation prediction of metal ion and humic and
 fulvic substances (Romero and Joensson 2005; Unsworth, Warnken et al. 2006).
 For this study all DOC was assumed to consist of humics. A sensitivity analysis of
 the humic complexation model was conducted by altering the fulvic:humic acid
 190 ratio in the model, setting the value 1, 0.95, 0.9, 0.75 and 0.4 in repeats of
 simulation.

Table 2. Physico-chemical parameter average values measured in the gully pot during the exposure period.

Sampling period	pH	conductivity (mS m ⁻¹)	DOC (mg l ⁻¹ C)
7 days	7.95	198.4	2.90
14 days	7.89	189.7	3.33

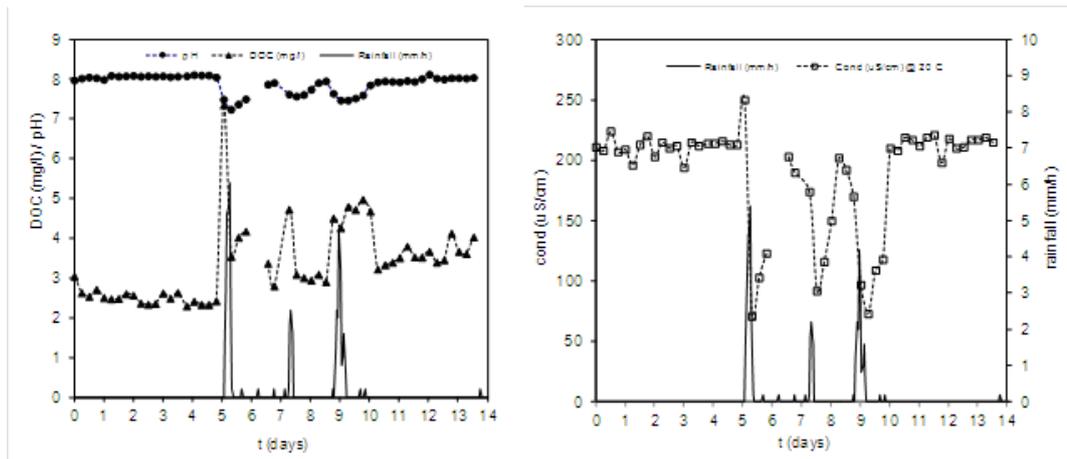
195 Table 3. Principal components average concentration in surface run off water and input parameters used in the visualMINTEQ calculations.

Period average	Cl ⁻	SO ₄ ²⁻	NO ₃ ⁻
7 days (mg l ⁻¹)	41	32	6
14 days (mg l ⁻¹)	39	31	6

200 The input parameters used for the visualMINTEQ calculations can be seen in
 Table 2 and Table 3.

Results and discussion

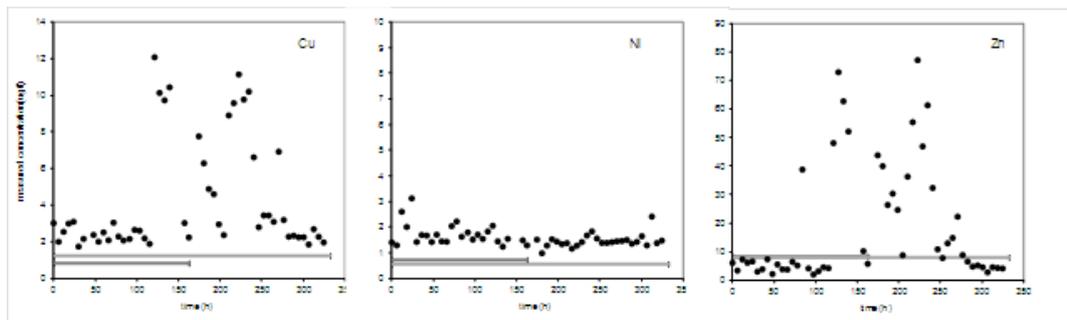
Passive samplers were deployed in a gully pot for 7 and 14 days, respectively.
 Water samples were collected by a time controlled automated sampler, resulting
 205 in 52 pooled water samples that were analysed for bulk parameters and dissolved
 metals. During the deployment there were three larger rain events taking place
 (see Figure 2). The precipitation resulted in identifiable peaks in DOC and metal
 concentrations, and dips in the conductivity (see Figure 2 and Figure 3). This
 observation was expected as particles and solid residue that had accumulated on
 210 surrounding hard surfaces was washed away and flushed into the storm water
 system (Boller and Steiner 2002).



215 Figure 2. DOC and pH (left panel) and conductivity (right panel) measured in the sedimentation chamber during the deployment period. Rainfall data (Website 2007) has been superimposed in both panels.

Since peaks in dissolved Cu and Zn concentrations (<0.45µm) coincided with the rain events, it is reasonable to assume that these metals were washed and transported to a large extent by the rainwater as freely dissolved ionic species, and small colloidal complexes that were not excluded by the filtration pretreatment.

220 For Ni no identifiable peaks that can be associated with the rain events could be observed, indicating either that Ni was mobilized only to a small extent by the rainwater, or that it was attached to larger particles that rapidly were deposited to the bottom (see Figure 3).



225 Figure 3. Concentration of dissolved species from automatic spot sampling (dots) and TWA concentrations derived from the passive sampler (lines) for 7 and 14 days, respectively. Cu, Ni, and Zn from left to right.

The metal speciation model visualMINTEQ was used to predict metal speciation. The NICA-Donnan model, incorporated in the visualMINTEQ software, was selected to estimate metal interactions with humic substances present in the water. 230 The entire DOC was assumed to consist of humic substances. Since the composition of the humics was unknown, several cases were tried where the fulvic acid (FA) to humic acid (HA) ratio was adjusted as an input parameter in

the model. From the results it was evident that visualMINTEQ predicts the free
235 ionic Cu to be <0.01%, while >99.9% was bound to FA and HA complexes,
regardless of the FA:HA ratio entered in the model (see Figure 4). The situation
was slightly different for Ni, for which predicted free ionic species decreased from
64.5% to 48.2% as the FA:HA ratio was lowered from 1 to 0.4. The Zn speciation
prediction proved even more sensitive to FA:HA variations with the predicted free
240 ionic form Zn decreasing from 82.3% to 43.2%. Overall, both model predictions
and passive sampler derived concentrations indicated that only a fraction of the
dissolved metals were present in freely dissolved or passive sampler labile form.
This is in line with expectations and what has been reported in the literature
(Blom, Morrison et al. 2002; Unsworth, Warnken et al. 2006).

245 Theoretically, passive samplers accumulate free ionic species, and other species
that are weak enough to dissociate within the timescale of the diffusion
process(Li, Zhao et al. 2005). This statement is in agreement with what is
observed for Cu, as the concentration reported by the passive sampler (0.83 ± 0.16
 $\mu\text{g L}^{-1}$) is much higher than the concentration of free ionic species predicted by
250 visualMINTEQ (0.011%, or $\sim 0.4 \text{ ng L}^{-1}$), as can be seen in Figure 4.
The free ionic Ni concentration predicted by the model is slightly higher (40-53%)
than the concentration reported by the passive samplers. A possible explanation
for this is that there were insoluble Ni-oxides or other insoluble Ni species present
that were not predicted by visualMINTEQ, although it should be noted that the
255 difference largely falls within the standard deviation of the passive sampler
measurement.

The model speciation output for Zn showed much greater sensitivity to variation
in the FA:HA ratio. This makes interpretation difficult, but in the case with
FA:HA ratio of 40:60 the model predictions agreed fairly well with the passive
260 sampler results.

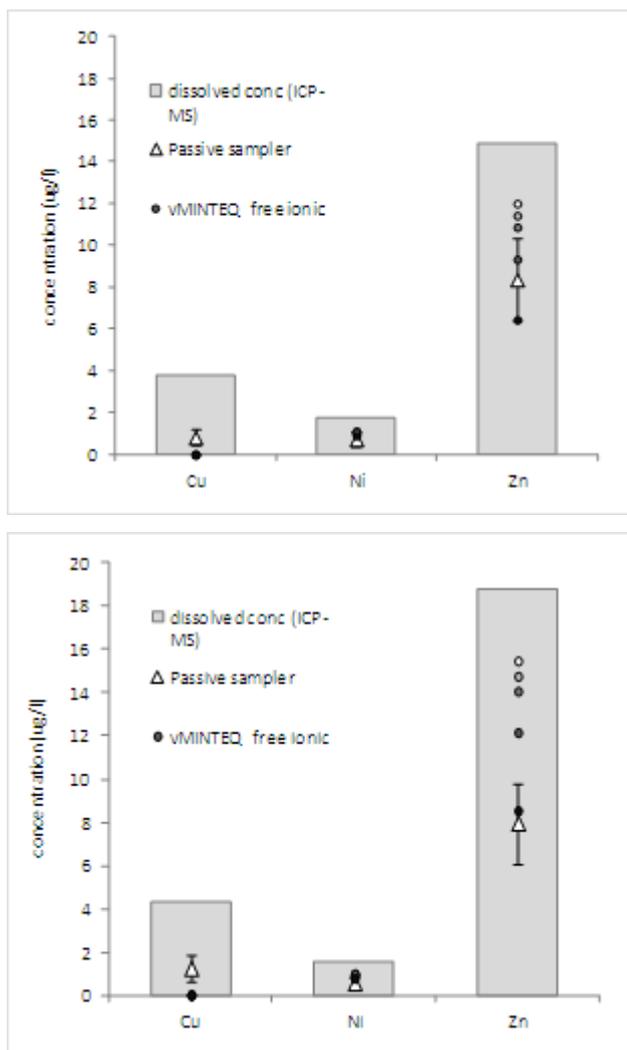


Figure 4. Concentration results for the 7 day (left) and 14 day deployments (right) of passive samplers (Δ) compared with total dissolved concentration from pooled samples (bars) and speciation code predictions for FA:HA ratios, ranging from 1 (o) to 0.4 (\bullet).

265 The comparison of measured and modeled data (Figure 4) suggests that the passive sampler accumulates other species than the freely dissolved fraction, which was predicted to be near zero in modeled cases. This can be explained if we consider that the metal species available for the passive sampling system are the:

270 (a) free metal ions that readily diffuse through the diffusion layer and accumulate on the receiving phase, (b) metal complex species that can dissociate within the diffusive time-scale in the diffusion layer and (c) metal complexes resulting from the exchange reaction between metal ligands and functional groups on the receiving phase. Metal complex species that are inert to the receiving phase and/or

275 subject to size discrimination are not considered labile and will therefore be excluded from further discussion (Li, Zhao et al. 2005).

Of the labile species, the group of metal complexes able to dissociate within diffusive layers (b) is of most interest for the present study and will therefore be discussed in detail below. Under certain circumstances it is conceivable that the metal complexes sampled through mechanism (b) will dominate the accumulation depending on the total diffusional pathway (e.g. Cu in the presence of humic substances, with >99% Cu-DOC complex form and a long diffusional pathway, see Figure 5). Increased thickness will facilitate the accumulation of species with relatively low dissociation rates, since the residence time of the species in the diffusive gel will increase, whereas decreased thickness will lead to accumulation of species only with high dissociation rates (Scally, Davison et al. 2006).

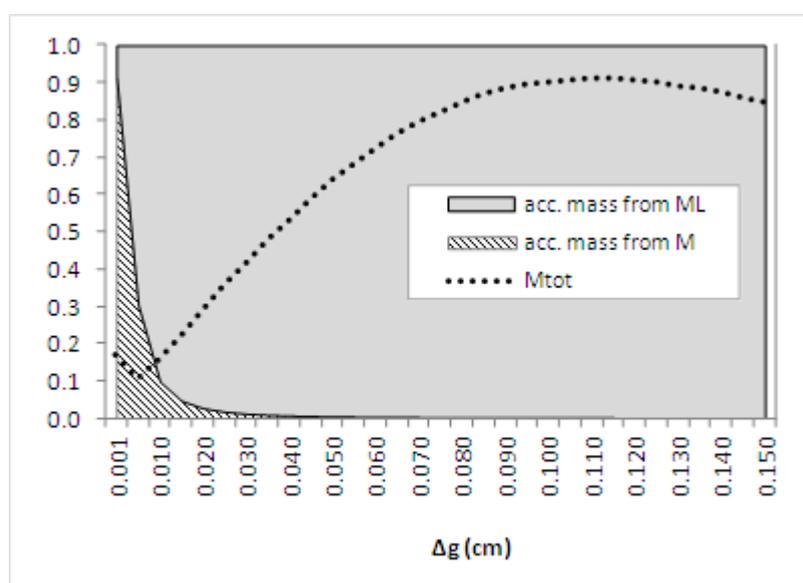


Figure 5. Theoretical distribution of accumulation on a passive sampler for a metal that is >99% in the ligand form (ML) and <1% in free ionic form (M). The graph also shows the total accumulated mass using an arbitrary scale.

On a more general level it should be pointed out that while speciation codes that computes speciation in equilibrium does not fully describe the situation in natural systems that are usually characterized by chemodynamic non-equilibrium, i.e. ongoing chemical reactions and transformations that are kinetically rate limited (Buffle, Wilkinson et al. 2009). Thus, it is unreasonable to expect such equilibrium models to perfectly predict the speciation in a non-equilibrium system. On the other hand, the passive sampler is providing a record of the dynamic processes for the duration of its deployment, making it a better tool for estimating the free ionic metal activity.

Using a combination of automated sampling, speciation model software and passive sampler, we could obtain total and soluble metal concentrations, labile

metal concentrations and free ionic species concentrations. Such a combination can provide detailed insights about metal speciation in the storm water system. Passive samplers can provide labile metal concentrations with relatively simple
305 sampling procedures and low costs. Passive samplers are therefore interesting alternatives for monitoring program.

This study shows that passive samplers collect labile metals species, as well as weak metal complexes. Such species are relevant to monitoring of metal fluxes, as they are often more bioavailable and, therefore, present the greatest risks for
310 human health and the environment.

In future studies it would be useful to include of a model for calculating fluxes and dynamic speciation, such as FLUXY or MHEDYN (Alemani, Buffle et al. 2008; Zhang, Buffle et al. 2008) and that are currently under development, to further close the gap between theoretical prediction and empirical observation for
315 passive samplers.

Conclusion

Passive samplers were used to determine time weighted metal concentrations in a storm water treatment facility. It was assumed that passive samplers collect only a small fraction of the total metal concentration in the bulk water phase, in
320 accordance with theories about lability criteria. The passive sampler derived concentrations were significantly lower than arithmetic mean concentrations derived from pooled and filtered samples collected with an automated sampler. Computer based speciation code predictions partly agreed with passive sampler results, especially when taking into consideration the increased lability of metal-
325 humic complexes as the diffusion boundary layer thickness increases. These findings imply that passive samplers are a useful tool for the monitoring of freely dissolved metal species in urban runoff water. It is suggested that the emerging chemodynamic speciation codes might be a better framework for linking passive sampler derived concentrations with total metal concentrations, although this
330 suggestion remains to be explored.

Acknowledgements

We would to thank the local road and transportation authorities in Gothenburg for allowing access to the storm water treatment facility that was used for this study.

References

- 335 Alemani, D., J. Buffle, et al. (2008). "Metal flux and dynamic speciation at (bio)interfaces. Part IV: MHEDYN, a general code for metal flux computation; application to particulate complexants and their mixtures with the other natural ligands." Environmental Science and Technology **42**(6): 2028-2033.
- 340 Allan, I. J., J. Knutsson, et al. (2007). "Evaluation of the Chemcatcher and DGT passive samplers for monitoring metals with highly fluctuating water concentrations." Journal of Environmental Monitoring **9**(7): 672-681.
- Allan, I. J., J. Knutsson, et al. (2008). "Chemcatcher and DGT passive sampling devices for regulatory monitoring of trace metals in surface water." Journal of Environmental
- 345 Monitoring **10**(7): 821-829.
- Allan, I. J., B. Vrana, et al. (2006). "Strategic monitoring for the European Water Framework Directive." TrAC Trends in Analytical Chemistry **25**(7): 704.
- Allan, I. J., B. Vrana, et al. (2006). "A \"toolbox\" for biological and chemical monitoring requirements for the European Union's Water Framework Directive." Talanta **69**(2): 302-
- 350 322.
- Beckwith, P. R., J. B. Ellis, et al. (1986). "Heavy metal and magnetic relationships for urban source sediments." Physics of the Earth & Planetary Interiors **42**(1-2): 67.
- Bjoerklund Blom, L., G. M. Morrison, et al. (2002). "Performance of an in situ passive sampling system for metals in stormwater." Journal of Environmental Monitoring **4**(2): 258-262.
- 355 Björklund Persson, L., G. M. P. Morrison, et al. (2001). "Diffusional behaviour of metals in a passive sampling system for monitoring aquatic pollution." Journal of Environmental Monitoring **3**: 639-645.
- Blom, L. B., G. M. Morrison, et al. (2002). "Performance of an in situ passive sampling system for metals in stormwater." Journal of Environmental Monitoring **4**(2): 258-262.
- 360 Boller, M. A. and M. Steiner (2002). Diffuse emission and control of copper in urban surface runoff. Water Science and Technology. **46**: 173-181.
- Brown, J. N. and B. M. Peake (2006). "Sources of heavy metals and polycyclic aromatic hydrocarbons in urban stormwater runoff." Science of the Total Environment **359**(1-3): 145-155.
- 365 Buffle, J., K. J. Wilkinson, et al. (2009). "Chemodynamics and bioavailability in natural waters." Environmental Science and Technology **43**(19): 7170-7174.
- Dos Anjos, V. E., G. Abate, et al. "Comparison of the speciation of trace metals in freshwater employing voltammetry, Diffusive Gradients in thin films (DGT) and a chemical equilibrium model." ComparaÃ§Ã£o da labilidade de metais empregando voltametria, difusÃ£o em filmes finos por gradiente de concentraÃ§Ã£o (DGT) e modelo
- 370 computacional **33**(6): 1307-1312.
- Florence, T. M., G. M. Morrison, et al. (1992). "Determination of trace element speciation and the role of speciation in aquatic toxicity." Science of the Total Environment **125**: 1-13.
- Gustafsson, J. P. (2006). Visual MINTEQ. Stockholm, Royal Institute of Technology.
- 375 Legret, M. and C. Pagotto (1999). "Evaluation of pollutant loadings in the runoff waters from a major rural highway." Science of the Total Environment **235**(1-3): 143-150.
- Levy, J. L., H. Zhang, et al. (2012). "Kinetic signatures of metals in the presence of suwannee river fulvic acid." Environmental Science and Technology **46**(6): 3335-3342.
- Li, W., H. Zhao, et al. (2005). "Metal speciation measurement by diffusive gradients in thin films technique with different binding phases." Analytica Chimica Acta **533**(2): 193-202.
- 380 Li, W., H. Zhao, et al. (2005). "Trace metal speciation measurements in waters by the liquid binding phase DGT device." Talanta **67**(3): 571-578.
- Roig, N., M. Nadal, et al. (2011). "Novel approach for assessing heavy metal pollution and ecotoxicological status of rivers by means of passive sampling methods." Environment
- 385 International **37**(4): 671-677.
- Romero, R. and J. A. Joensson (2005). "Determination of free copper concentrations in natural waters by using supported liquid membrane extraction under equilibrium conditions." Analytical and Bioanalytical Chemistry **381**(7): 1452-1459.
- 390 Rule, K. L., S. D. W. Comber, et al. (2006). "Diffuse sources of heavy metals entering an urban wastewater catchment." Chemosphere **63**(1): 64.

- Runeberg, K. (2005). Chemcatcher :performance of a passive sampling system for aquatic monitoring of metals Department of Civil and Environmental Engineering, Chalmers University of Technology.
- 395 Scally, S., W. Davison, et al. (2003). "In Situ Measurements of Dissociation Kinetics and Labilities of Metal Complexes in Solution Using DGT." Environmental Science and Technology **37**(7): 1379-1384.
- Scally, S., W. Davison, et al. (2006). "Diffusion coefficients of metals and metal complexes in hydrogels used in diffusive gradients in thin films." Analytica Chimica Acta **558**(1-2): 222-229.
- 400 Tonello, P. S., D. Goveia, et al. (2011). "Determination of labile inorganic and organic species of Al and Cu in river waters using the diffusive gradients in thin films technique." Analytical and Bioanalytical Chemistry: 1-8.
- Unsworth, E. R., K. W. Warnken, et al. (2006). "Model Predictions of Metal Speciation in Freshwaters Compared to Measurements by In Situ Techniques." Environmental Science & Technology **40**(6): 1942-1949.
- 405 Warnken, K. W., A. J. Lawlor, et al. (2009). "In situ speciation measurements of trace metals in headwater streams." Environmental Science and Technology **43**(19): 7230-7236.
- Website. (2007). "Luftnet - väder och luftkvalitet i Göteborg." Retrieved March 28, 2007, from <http://www.miljo.goteborg.se/luftnet/>.
- 410 Zhang, H. (2004). "In-Situ Speciation of Ni and Zn in Freshwaters: Comparison between DGT Measurements and Speciation Models." Environmental Science and Technology **38**(5): 1421-1427.
- Zhang, Z., J. Buffle, et al. (2008). "FLUXY: A simple code for computing steady-state metal fluxes at consuming (bio)interfaces, in natural waters." Environmental Chemistry **5**(3): 204-217.
- 415