

THESIS FOR THE DEGREE OF DOCTOR OF PHILOSOPHY

Passive sampling for monitoring of inorganic pollutants in water

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Cover: A schematic representation of a Chemcatcher® passive sampler with principal components named.

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Abstract

As new environmental management policies for watersheds are implemented, there has been a growing interest for new monitoring alternatives. Traditionally grab sampling has been the method of choice for monitoring purposes, but may not be adequate or economically viable, to meet the requirements of the new policies.

Passive samplers for monitoring of aquatic pollutants have been described in the literature for almost three decades, but they are only beginning to gain acceptance outside the scientific research community. The potential advantages of passive samplers over other sampling and measurement strategies include the ability to integrate pollutant levels over extended sampling periods (up to several weeks), as well as inherent speciation capabilities, allowing for critical in situ speciation of metals. Passive samplers are relatively low-cost and do not require secure locations or additional infrastructure, making them ideal devices for certain monitoring tasks.

The research presented in this thesis aims at further developing passive sampling for aquatic monitoring. This research includes field trials, the development of a novel application for nutrient monitoring in waste water treatment plant effluents and the identification of scenarios for which passive samplers can be used. An analysis of measurement uncertainties associated with passive samplers is also presented.

Keywords: passive samplers, heavy metals, speciation, pollutant monitoring, natural water, urban run-off, waste water, WFD.

List of appended papers

The cover paper in this thesis is based on the following papers, referred to with roman numerals in the text:

Paper I: Allan, I.J., et al., Strategic monitoring for the European Water Framework Directive. Trends in Analytical Chemistry, 2006. 25(7): p. 704.

Paper II: Allan, I.J., et al., Evaluation of the Chemcatcher and DGT passive samplers for monitoring metals with highly fluctuating water concentrations. Journal of Environmental Monitoring, 2007. 9: p. 672-681.

Paper III: Allan, I.J., et al., Chemcatcher and DGT passive sampling devices for regulatory monitoring of trace metals in surface water. Journal of Environmental Monitoring, 2008. 10(7): p. 821-829.

Paper IV: Vrana, B., et al., Passive sampling techniques for monitoring pollutants in water. TrAC, Trends in Analytical Chemistry, 2005. 24(10): p. 845-868.

Paper V: Knutsson, J., et al. Evaluation of a passive sampler for the speciation of metals in urban runoff water. Submitted to Environmental Science: Processes & Impacts.

Paper VI: Knutsson, J., S. Rauch, and G.M. Morrison, Performance of a passive sampler for the determination of time averaged concentrations of nitrate and phosphate in water. Environmental Science: Processes & Impacts, 2013.

Paper VII: Knutsson, J., et al. Estimation of measurement uncertainties for passive samplers used in water quality monitoring. Submitted to Analytical chimica acta.

Other published work by the autor:

Arpadjan, S. ; Tsekova, K. ; Petrova, P. et al. (2012). Field sampling, speciation and determination of dissolved iron (II) and iron (III) in waters. Bulgarian Chemical Communications. 44 (4) p. 299-306.

Arpadjan, S. ; Petrova, P. ; Knutsson, J. (2011). Speciation analysis of thallium in water samples after separation/ preconcentration with the Empore TM chelating disk. International Journal of Environmental Analytical Chemistry. 91 (11) p. 1088-1099.

Kalmykova, Y. ; Knutsson, J. ; Strömvall, A-M. (2009). Blast-Furnace Sludge as Sorbent Material for Multi-Metal Contaminated Water. S. Rauch, G.M Morrison and A.Monzon, Highway and Urban Environment, Madrid, Springer. p. 325-336.

Mills, G. A.; Allan, I. J.; Guigues, N.; Knutsson, J.; Holmberg, A.; Greenwood, R. (2009). Monitoring heavy metals using passive samplers. Rapid chemical and biological techniques for water monitoring. p. 243-262. ISBN 978-0-470-05811-4

Arpadjan, S.; Petrova, P.; Knutsson, J. (2008). Preconcentration Methods for Determination of Thallium in Natural Waters. Eurasian Journal of Analytical Chemistry, 3 (1)

Rauch, S. ; Knutsson, J. (2007). The relative impact of automobile catalysts and Russian smelters on PGE deposition in Greenland. Highway and Urban Environment, Morrison G.M. and Rauch S. (Eds). p. 215-222.

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Glossary

Chemcatcher [®]	A patented kinetic passive sampling device with a receiving phase comprising a commercially available extraction disk.
DBL	Diffusion Boundary Layer. Referring to the stagnant layer at the water-passive sampler interface where primary transport of analyte is through diffusion
DGT	Diffusive Gradients in Thin films. A patented kinetic passive sampling device with a receiving phase consisting of Chelex resin incorporated in an agarose gel disk
Diffusion	In chemistry diffusion is used to describe the process of net transport of a compound from a high to a low concentration compartment that occurs due to random movement of molecules in the media
Diffusion layer	The nominally inert and stagnant compartment of a passive sampler where the transport of analyte towards the receiving phase occurs through diffusion.
DOC	Dissolved organic carbon. Refers to a fraction of dissolved organic matter in water.
FA	Fulvic acid, a fraction of (usually natural) organic acids that is a part of the group Humic substances.
Grab sampling	The act of collecting a discrete (water) sample for either on site analysis or to be transported to a laboratory for subsequent analysis.
HA	Humic acid, a fraction of (usually natural) organic acids that is a part of the group Humic substances.
ICP-MS	Inductively coupled plasma – mass spectrometry, an analytical technique which allows for detection and quantification of trace level elements in various types of matrices.
NOM	Natural organic matter Refers to a fraction of organic matter of natural origin in water.
Receiving phase	The compartment of a passive sampler that is acting as a recipient or sinks for the analytes(s) through chemical affinity.
Speciation	Refers to the the distribution of a compound among its chemical species /forms.
TWA	Time Weighted Average.
WFD	The Water Framework Directive, a policy programme for management of water bodies in the EU
WWTP	Waste Water Treatment Plant.

Acknowledgements

“Research is what I'm doing when I don't know what I'm doing.”

Verner von Braun

According to the great wisdom of Dr. Braun, I indeed seem to have spent a great deal of my time in this project doing research, but as anyone involved in science knows, not much can be accomplished without the support of others. Therefore it is in place to mention, in no special order, some of all the people who have helped, supported and in other ways contributed to my journey.

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May those who are not mentioned here forgive me, and know I will always be thankful to all those who have helped me.

Gothenburg, May 2013.

1 Introduction

Water is used by humans for consumption and utility, and we rely on access to clean, safe water for almost all aspects of our societal functions. Throughout history water has also acted as a waste transport medium carrying away the byproducts of our settlements and dispersing them into the environment. As populations and settlements grew larger, and the types of waste we produced became increasingly alien to the natural environment, the problem of water pollution with endemic environmental degradation also became apparent.

The pressure induced from the unsustainable use and pollution of water, together with population growth and the globally uneven distribution of fresh water resources, has in some regions already resulted in ecological and societal collapse, with many more being at severe risk [1, 2].

It is therefore of utmost importance to preserve and safeguard the remaining water resources, and to ensure their sustainable management. This includes the responsible usage of water, but also monitoring of the chemical and ecological status of surface and ground water sources. Environmental monitoring of water is therefore becoming increasingly important in a world with an ever growing appetite for resources. Ambitious policy programs on water management have been adopted by authorities around the globe (e.g. the Water Framework Directive, Directive 2000/60/EC). However, financial constraints still limit monitoring activities, which makes the development of cost-efficient monitoring techniques important.

Three basic approaches can be used for the environmental monitoring and measurement of water.

Traditionally the most commonly used approach has been bottle or grab sampling, with subsequent storage and laboratory analysis. Though widely used, this approach is associated with a number of commonly acknowledged drawbacks [3, 4](Paper I), including high cost, the introduction of artifacts from transport and storage of the sample and the fact that grab sampling gives only a snapshot of the water status in the investigated water. The latter can be addressed by the use of automated grab sampling, but this approach is associated with problems of its own, in that it is being relatively complicated and expensive and requires access to a secure location and suitable infrastructure (e.g. electricity).

The aforementioned drawbacks are of particular concern for trace elements where speciation changes may add bias to the assessment for water bodies with fluctuating analyte levels.

An alternative approach in water monitoring is to measure the analyte immediately after the sampling (on-site but off line), which eliminates most of the issues associated with sample storage. If the analysis is done on-line, continuously or sequentially, this allows for close to real time mapping of spatial and temporal variations of the analyte. In-field type analysis is often performed using traditional laboratory techniques, though sometimes modified and adapted to conditions in the field [3].

The third approach is sampling by *in situ* measurements, which refers to analyses performed directly in the environmental compartment of interest (i.e. at the desired time, depth and location). This avoids most of the issues with the sampling, where changes in light, temperature, pressure and redox conditions may compromise the sample.

1.1 *In situ* techniques

In situ analysis methods have improved significantly in recent decades, and it is expected that this rapid development will continue in the future, enhancing our ability to understand and model ecosystems, and thereby making us better able to protect them.

In situ techniques can be divided into three distinct groups, one of which is *continuous in situ sampling*. This group of *in situ* techniques comprises electrodes that provide a

continuous response to analyte concentrations in the water; examples include pH and ion selective electrodes. The second group contains techniques that provide series of *in situ discrete measurements*, including voltammetric and flow injection analysis techniques. In the last group, fractionation and accumulation of the analyte occurs in situ, but the analysis of the accumulated fraction is carried out in a subsequent step at the laboratory [5, 6]. This group includes passive samplers which are the subject of this thesis.

1.2 Passive samplers

Passive sampling techniques have been used for the determination of a wide range of analytes in various applications in air, water and soil for almost three decades [7].

In the aquatic environment passive sampling has been used to determine concentrations, fluxes and lability of metals [8-17], anionic species [18-21, 22], a wide range of organic pollutants [23, 24] (including pharmaceuticals [25] and endocrine disruptors [26]), as well as organo-metallic compounds [27].

One major advantage of passive sampling as a technique is its inherent specificity towards the analyte of interest. Generally, a passive sampler device will only sample a fraction of the total analyte present; freely dissolved species and labile complexes as well as conjugated species. More specifically, this means those species that would dissociate within the timescale of transport across the diffusion pathway of the sampling device, and that have a stability constant lower than the stability constant of the compound formed as a result of the binding to the samplers receiving phase.

The fraction accumulated by passive sampling reflects the analyte's behavior in the investigated environment, yielding valuable information not only on its content but also on its chemical status (the different species present, speciation), thereby contributing to the more accurate assessment of the environmental impact of the analyte [28] (e.g. the metal concentrations assessed with a passive sampler correlates to the biologically relevant fraction of the metal in the studied environment).

Even though passive sampling technique is commonly used as a research tool, water passive samplers are still not widely recognized for environmental regulatory monitoring.

In recent years passive sampling in aquatic environments has been shown to provide information about the average water quality that in some aspects is more reliable than information obtained with infrequent grab sampling (even assuming a lower degree of uncertainty with the single determination) (Paper II-III). Thus, the passive sampler technique should meet the criteria stated for example in the Water Framework Directive of the European Commission (Directive 2000/60/EC) that data have to be representative and intercomparable.

1.3 Aims and objectives

The aim of this work was to evaluate the suitability of the passive sampler for environmental monitoring in the context of a regulatory framework (WFD), and its performance in applied monitoring situations in different compartments, such as rivers, storm water runoff and wastewater effluent. Different types of passive sampler types and configurations were investigated, both in terms of compliance to the requirements in the water framework directive (WFD) (papers I-III) and in terms of speciation capabilities (papers V-VI).

2 Principles of the passive sampler

The term “passive sampler” covers several distinct subgroups of. These can be classified according to the sampling medium (gaseous or aqueous), the operating mode (equilibrium or kinetic) and the target class of analyte (organic or inorganic, see Figure 1).

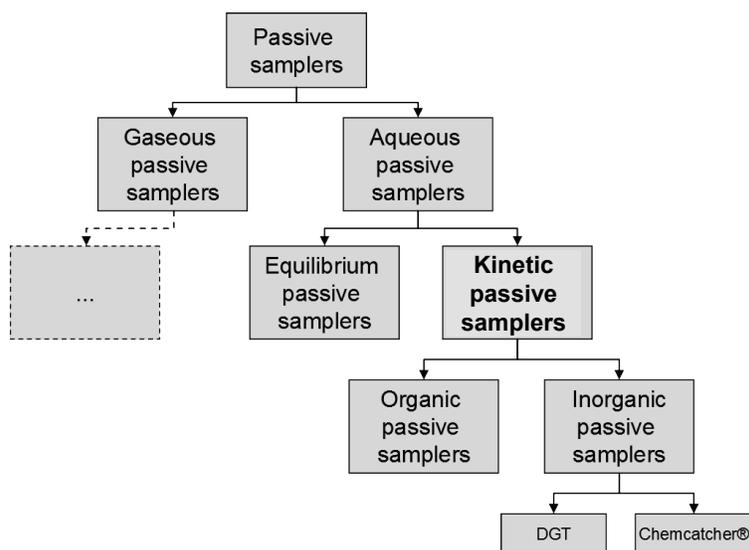


Figure 1. Tree view of the hierarchical categorization of passive sampling techniques.

In equilibrium passive sampling, as the name suggests, the analyte(s) are accumulated in the device until the concentration in the sampler is in equilibrium with the bulk concentration, one example is Donnan-dialysis, used for metal ions sampling [29, 30]. This type of passive sampler is typically used to provide a snap shot of the labile analyte concentration at the moment of sampling, although in practice there is a response lag time before equilibrium is reached if there is a change in concentration.

The kinetic passive sampling devices are designed to continuously accumulate the analyte by maintaining a concentration gradient and a mass flux of analyte over the course of the exposure. Kinetic passive samplers are in some ways a special case of equilibrium passive samplers where the sampling medium has been chosen so that the water-sampler partition coefficient is large, and/or by assuring a large capacity of the receiving medium. Another difference is that it is generally desirable that the mass flux between the sampler and the bulk water compartment is slowed down, so that the time to equilibrium (saturation) is sufficiently long to allow extended sampling in the kinetic regime.

The techniques based on kinetic passive sampling are conceptually similar, even though there are some exceptions. Examples of kinetic passive samplers used for inorganic analytes includes DGT [4], Chemcatcher[®] [8], SLMD [31] *etc.*

The Chemcatcher[®] passive sampler was developed by researchers from Portsmouth University and Chalmers University of Technology. It has been described in a number of different configurations for different target analytes, including polar [23, 32] and non-polar [33] organic compounds, metals [8, 9, 34] (Paper V) and inorganic anions (Paper VI). All configurations of the Chemcatcher[®] comprise a plastic sampler body, a commercially available solid phase extraction disk as a receiving phase and a, for the target analyte suitable, diffusion limiting membrane (see Figure 2).

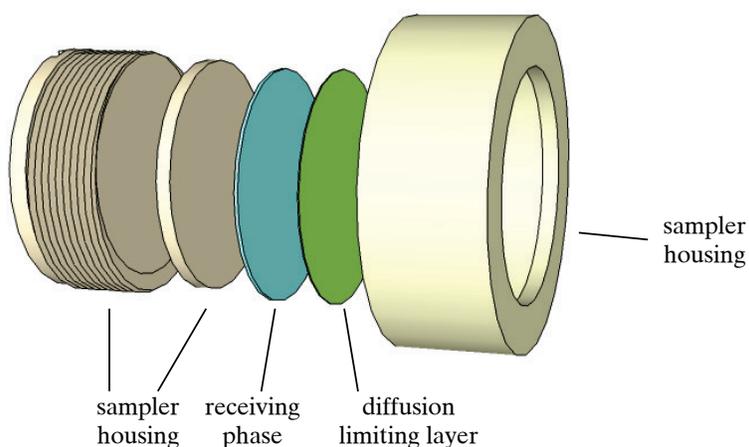


Figure 2. Schematic 3D render of the Chemcatcher[®] passive sampler showing the principal components.

The Diffusive Gradients in Thin films (DGT) technique was developed by researchers at Lancaster University. It comprises a plastic sampler body of a single-use piston type, a receiving phase that consists of a solid resin cast in agarose gel (usually Chelex resin) and a diffusion limiting layer cast in agarose gel using different modifiers to regulate gel pore size (see Figure 3). The vast majority of the published work on DGT relates to metal analysis and speciation using a standard configuration, but other configurations have been reported, for example the use of ferrihydrite to accumulate phosphorous [21, 35] and a DGT device where the agarose gel media was exchanged for paper based media [18].

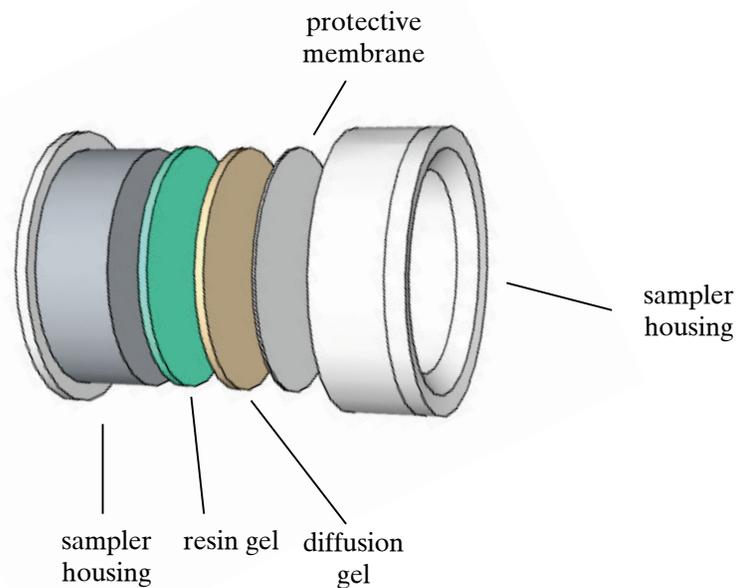


Figure 3. Schematic 3D render of a DGT passive sampler showing the principal components.

2.1 Kinetic passive sampling

Passive samplers used in the kinetic accumulation mode usually have a receiving phase with a strong affinity for the analyte and a large capacity, thereby effectively creating a sink. The adsorption of the analyte on the receiving phase sustains the concentration gradient driving the diffusion of analyte species [4, 9, 36]. Normally it is assumed that a) there are no interactions between the diffusing species and the medium of the diffusive layer, b) the receiving phase maintains the concentration at the interface at effectively zero and c) the adsorption of the analyte species occurs in a plane sheet. The assumptions

made in a, b and c have been shown to hold for the most common condition encountered [37-41].

The accumulation curve for a device in the kinetic phase consists of a linear section and a non-linear section, where the accumulation rate decrease, to eventually reach zero when equilibrium/saturation is reached (see Figure 4). Optimally, the exposure of the sampler is terminated before the non-linear stage is reached.

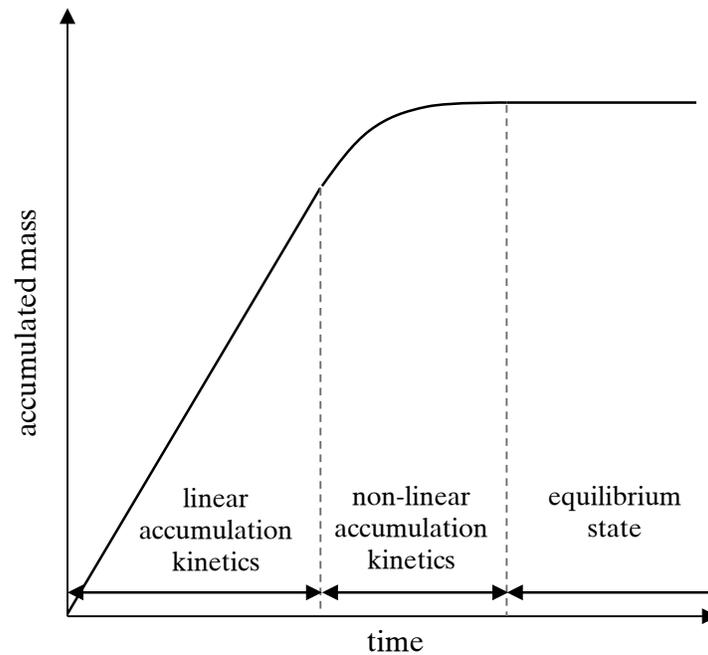


Figure 4. Schematic representation of the different accumulation regimes during exposure of a passive sampler.

As the analyte is adsorbed on the receiving phase the local analyte concentration is lowered and a concentration gradient is established. The accumulation rate is limited by the speed of the analyte diffusion through the diffusion pathway, which is described by the diffusion coefficient, D ($m^2 s^{-1}$), and by the total length of the diffusion pathway. The diffusion coefficient is described theoretically by the Stokes-Einstein equation:

$$D = \frac{k_b T}{3\pi\mu d} \quad \text{Equation 1}$$

where k_b is the Boltzmann constant ($1.38 \times 10^{-23} \text{ J K}^{-1}$), T is the temperature (K), μ is the dynamic viscosity ($\text{g s}^{-1} \text{ m}^{-1}$) and d is the ionic diameter of the analyte (m).

The diffusion pathway is made up of two components. One component is the diffusion limiting layer which may consist of a porous solid media, like an agarose gel (in the case of DGT) or a membrane filter (in the case of Chemcatcher®). The other component of the diffusion pathway is an aqueous diffusion boundary layer (DBL).

2.2 Diffusion limiting layer

In kinetic passive sampling it is generally desirable to have a diffusive layer of well-defined thickness to lessen the impact of variations in water turbulence. This, among other things, can be accomplished by introducing a diffusion limiting layer. The diffusion limiting layer can for example consist of a polymer gel [4, 42] or a cellulose acetate membrane filter [8, 34]. The diffusion limiting layer can also have other functions, such as to exclude analyte species that are too large to pass through the pores, and to reduce the sampler sensitivity to variations in turbulence.

2.3 Diffusion boundary layer

The DBL is a pseudo-stagnant layer that forms at the interface between the passive sampler and the sampled media. The DBL is a gradient where the water movement decreases as the distance to the passive sampler surface decreases. For practical purposes this layer will appear and be conceptually treated as a homogenous layer with a thickness which is a function of the bulk water turbulence (see Figure 5).

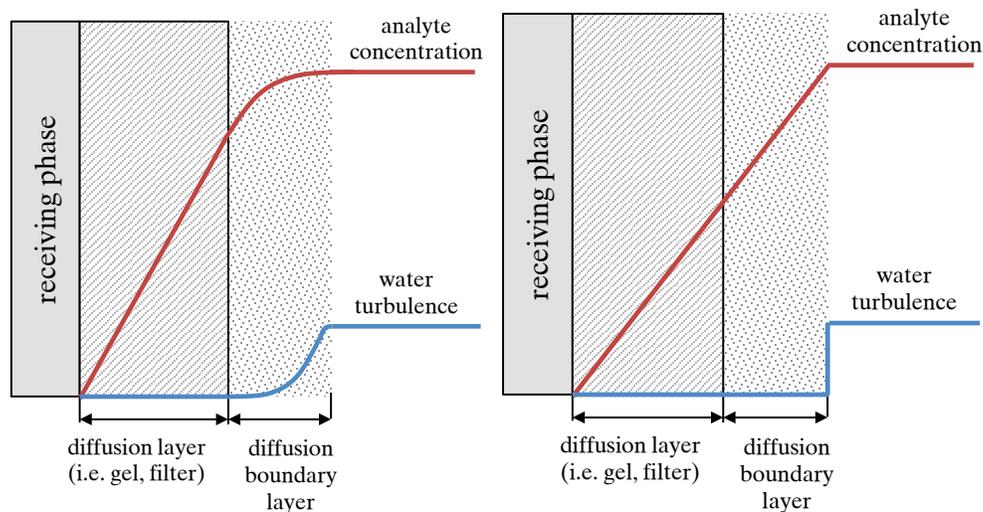


Figure 5. Schematic representation of the physical concentration gradient and the water turbulence gradient established at the passive sampler-water interface at steady state (to the left) and a simplified conceptualization where the DBL is treated as a homogenous part of the diffusion layer (to the right).

2.4 DGT model equation

In well mixed conditions the aqueous boundary layer can be disregarded if the diffusion limiting layer is sufficiently thick, and the accumulated mass M can be calculated through

$$M = \frac{DCAt}{\Delta g} \quad \text{Equation 2}$$

where D ($\text{m}^2 \text{s}^{-1}$) is the diffusion coefficient of the species in the diffusion layer, C (g L^{-1}) is the labile analyte concentration in the bulk phase, A (cm^2) is the area of the diffusion plane, t (s) is time and Δg is the thickness of the diffusion pathway [5]. This approach, which is used with the DGT devices, requires knowledge of the diffusion coefficient for the temperature in which the sampler is going to be deployed. Diffusion coefficients can be found in the literature, or alternatively determined experimentally under laboratory conditions.

In situations where water turbulence is low, or where there is a need for more accurate results, the DBL should be taken into account. In a laminar flow conditions the thickness of the diffusion boundary layer (DBL) δ , can be estimated by the following equation

$$\delta \approx 3.3 \left(\frac{D}{\nu} \right)^{\frac{1}{3}} \left(\frac{\nu x}{U} \right)^{\frac{1}{2}}$$

Equation 3

where D ($\text{m}^2 \text{s}^{-1}$) is the diffusion coefficient, ν is the kinematic viscosity, x is the distance (m) from the leading edge and U (m s^{-1}) is the water velocity. Using this estimate it becomes evident that the DBL thickness is sensitive to changes in U for velocities lower than 1 cm s^{-1} , but less so for velocities over 2 cm s^{-1} (see Figure 6). This means that in stagnant or nearly stagnant conditions the DBL has to be considered in order to obtain reliable results from passive sampler measurement [43].

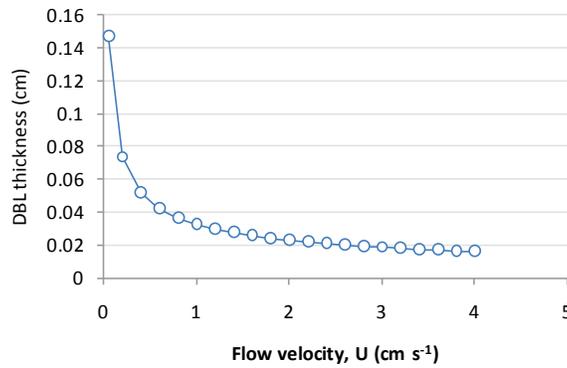


Figure 6. Graph showing the thickness of the diffusion boundary layer as a function of the laminar flow velocity, estimated by Equation 3 ($T = 20^\circ \text{C}$, $x = 1 \text{ cm}$).

It is, however, fairly straightforward to include the DBL into the calculation. The diffusion in the DBL can be considered to be an ordinary Fickian diffusion and the same relationship applies as for the pure diffusion layer:

$$M = \frac{D_g C_g A_s t}{\Delta g} + \frac{D_w (C_b - C_g) A_g t}{\delta}$$

Equation 4

Two areas are used here, as the effective sampling area is larger than the opening in the sampler body due to lateral diffusion of the analyte [44]; A_s denotes the area of the interface between the binding phase and the diffusion layer, while A_g denotes the bulk phase-diffusion layer interface. It then follows from elimination of C_g that:

$$M = \frac{A_s A_g D_w D_g t C_b}{A_w D_g \delta + A_g D_w \Delta g} \quad \text{Equation 5}$$

By simultaneously deploying samplers with varying diffusion layer thickness it is possible to construct a response curve, plotting Δg against the accumulated mass M . Equation 5 can then be fitted to the response curve by solving it for C_b and δ [43] using the least squares method.

Investigations into this approach have shown that in reasonably well stirred conditions (laminar velocity $> 2 \text{ cm s}^{-1}$) the DBL will be less than 0.2 mm thick, and δ can be disregarded without significant loss of accuracy [38].

However, in stagnant conditions, and/or when very high accuracy is needed, simultaneous deployment of samplers with different diffusion layer thickness should be considered [43, 44].

2.5 Chemcatcher® model equation

For the Chemcatcher® another way to express the accumulation on a passive sampler device was chosen [32]:

$$M = R_s C t \quad \text{Equation 6}$$

where the sampling rate, R_s (ml day^{-1}), of the device is an engineering term which incorporates the diffusion coefficient (D), the area of the diffusion plane (A) and the thickness of the diffusion layer (Δg). This simplification is valid, as these terms for practical purposes are assumed to be constant. For a given analyte, sampler device and under constant environmental conditions it is possible to perform laboratory calibrations to determine the sampling rate, which is then applicable for this exact set of conditions. During sampler exposure, fluctuations in environmental factors such as turbulence in the bulk phase will affect the thickness of the aqueous diffusion boundary layer (DBL) (and thus the total Δg), while changes in temperature will affect the diffusion coefficient D . The greater the deviation from conditions under which the sampling rate (R_s) was determined, the greater the error in the determination will be. It is therefore important to

use calibration data that is valid for the conditions under which the sampler is being deployed.

2.6 Calibrating for environmental variables

The Chemcatcher[®] passive sampler is calibrated for a set of environmental conditions where the effect of DBL thickness and changes in the diffusion coefficient are reflected in the resulting accumulation rate, or sampling rate (R_s). The sampling rate term (R_s) incorporates the effect from all environmental variables, and is a more simplified application than the DGT technique. However, the accuracy of such an approach relies on access to suitable (matching) and robust calibration data. In Table 1 examples of sampling rates for 40 rpm and 18 °C are shown.

Practical experience has shown that the Chemcatcher[®] is somewhat lacking in accuracy and precision compared to the DGT. A typical C_{DGT} / C_{ICP-MS} ratio for sampling of simple inorganic species in laboratory conditions is $0.99 \pm 0.051 - 1.05 \pm 0.066$ [43, 44], while for the Chemcatcher[®] this ratio is typically between 0.95 ± 0.10 (unpublished data of the author).

Table 1. Sampling rates with associated standard deviations for the Chemcatcher[®] passive sampler in 18 °C and 40 rpm setting on the turntable sampler holder.

	R_s (ml h ⁻¹)	RSD
Cd	4.4	14%
Cu	3.5	15%
Ni	3.5	12%
Zn	4.4	13%

2.7 Comparison with traditional sampling

Traditional sampling and analysis of metals in natural waters combine grab sampling with the subsequent work-up and analysis in the laboratory. This approach is associated with a number of disadvantages that can make the determination of metals and particularly their equilibrium speciation distribution erroneous. When taking a grab sample the composition of the sample may be altered at any time during the procedure of

sampling, transportation, preservation, storage and work-up, and while the magnitude of this perturbation may be minimized, it cannot be eliminated completely.

Recombination of metal species may take place as colloids can break up and oxides form due to changes in dissolved oxygen levels, redox conditions, pH and temperature as the sample is collected. Furthermore, there is always a risk for contamination, analyte loss or recovery problems.

In addition, grab sampling provides only instantaneous data, and when monitoring for regulatory purposes the use of infrequent grab sampling may result in a non-representative estimate of the pollution load status of the water body. If the analyte concentration fluctuates, grab sampling may either miss recurring pollution episodes, and therefore underestimate the total pollution load, or catch a pollution episode as it occurs, and possibly overestimate the total pollution load – if the results from such sampling is extrapolated to represent the pollution status of the sampled water body (see Figure 7).

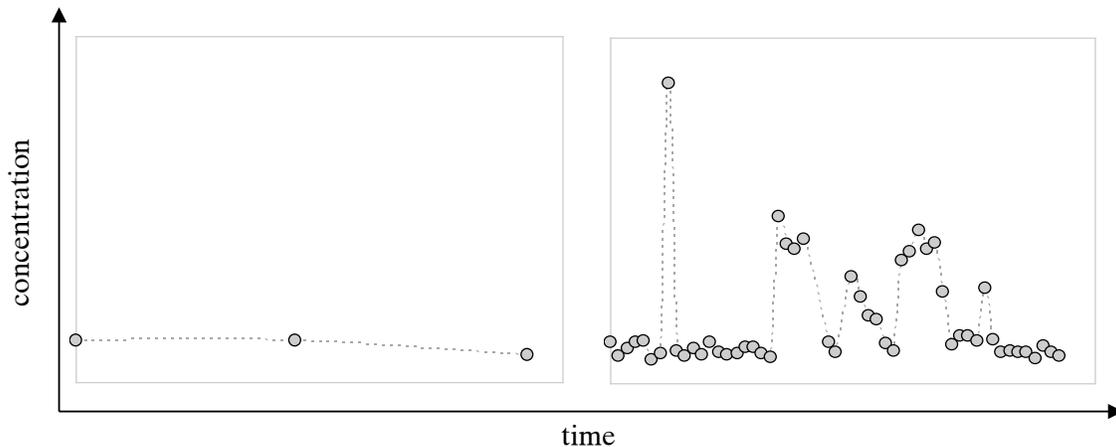


Figure 7. Variation of dissolved Cu levels in urban storm water determined by grab sampling (left panel) and frequent automated grab sampling (right panel).

To address the problem with fluctuating pollutant levels, frequent grab sampling can be used, where sampling interval is sufficiently short as to detect sporadic events. This is commonly solved by using automated sampling where samples are extracted triggered for example by a programmed timer or a flow-proportional trigger. This does not, however, address the other drawbacks with grab sampling outlined above.

All issues discussed above contribute to the sampling uncertainty. Generally, uncertainty in sampling can be described by the following terms of variance:

$$s_{total} = \sqrt{s_{\text{sampling}}^2 + s_{\text{analysis}}^2} \quad \text{Equation 7}$$

The sampling uncertainty can in turn be broken down into

$$s_{\text{sampling}} = \sqrt{s_{\text{primary}}^2 + s_{\text{secondary}}^2} \quad \text{Equation 8}$$

where *primary* represents the variance associated with the choice of sampling frequency, location, technique and timing, and *secondary* sampling uncertainty includes variance from sample treatment, transport and preservation (Paper I). A more detailed discussion about uncertainty in passive samplers is given in section 6.6 and in Paper VII that is a part of this thesis.

The passive sampling technique will probably mitigate some of the factors that contribute to uncertainty, while introducing a few new ones. The variance caused by sampling frequency, sample transportation and preservation are all likely to be less for passive sampling when compared to grab sampling. On the other hand, uncertainties from environmental conditions such as temperature (diffusion coefficients) and turbulence (boundary layer thickness) are introduced. It is reasonable, however, to assume that the net sampling uncertainty for passive sampling is lower than that for grab sampling.

It could be claimed that information on total pollution load derived from grab sampling will have a level of uncertainty that is inversely correlated to the sampling frequency and the number of sampling spots. From this follows that it would be possible to decrease the uncertainty to the desired level by increasing the sampling frequency and the number of sampling locations, however this may not always be feasible.

Also, it may be difficult to determine what constitutes frequent enough sampling, as analytical considerations have to be weighed against economic restrictions in monitoring programs [45] (Paper I).

By using passive sampling devices it is possible to avoid some of the problems described above. Since accumulation, speciation and fixation of the analyte takes place in situ the risk of changes in metal speciation during sampling, transport and storage is eliminated.

Furthermore, due to the integrative nature of the accumulation of analytes on kinetic passive samplers they will provide a time weighted average concentration over the duration of the deployment, minimizing the risk of missing pollution episodes, something which could result in an unrealistic assessment of the water quality status.

A simple comparison outlining some common drawbacks and benefits of grab sampling, automated grab sampling and passive sampling is presented in Table 2. Depending on the specific monitoring task at hand, passive samplers may or may not be the preferred tool compared with grab sampling.

Table 2. Overview of inherent pros and cons for passive sampling, grab sampling and automated grab sampling.

	Passive sampler	Grab sampling	Automated grab sampling/frequent
Need secure location	No (+)	No (+)	Yes (-)
Need infrastructure	No (+)	No (+)	Yes (-)
Analyte loss during transport and storage	No (+)	Yes (-)	Yes (-)
Detection of episodic pollution event	Yes (+)	No (-)	Yes (+)
Identifies short term patterns in pollution concentration	No (-)	No (-)	Yes (+)
Determination of total concentrations	Sometimes (-)	Yes (+)	Yes (+)

3 Speciation in natural fresh waters

The chemistry of natural surface waters is complex due to the wide range of inorganic, organic and biological components that are present. There can be significant differences in chemistry between water bodies, but considerable temporal and spatial variation can also be observed within the same water body, for example due to seasonal variations and stratification. The overall chemistry of the water determines the chemical speciation of the substances present.

Speciation is an ambiguous term that can refer to

a) the distribution of the compound among its chemical species

or

b) a group of analytical procedures that allow the determination of a).

In this thesis, *speciation* is used in both meanings described above, and may thus refer to speciation as a property or as an analytical procedure.

It is well known that the speciation of an element often determine its behavior and fate in the aquatic environment, and from knowledge about its speciation its fate can often be predicted [46]. This can be exemplified by mercury (Hg), which in its simple ionic form (i.e. Hg^{2+}) is adsorbed only to a small extent (5-7%) in humans, compared to >95% adsorption of methylated mercury [47]. Another example is copper (Cu) which in aqueous solutions preferentially forms complexes with humic substances, and in the complex form is largely non-toxic to aquatic organism, however, the ionic form, Cu^{2+} , is bioavailable and thus potentially toxic, having a detrimental effect on hematological parameters, and enzyme activities in fish [48].

3.1 Metal speciation

The speciation of metals in a water body can conceptually be described as a series of equilibrium reactions between the free hydrated metal ion ($M(H_2O)_x^{2+}$), small size complexes, complexes with macro molecules, non-soluble particles, soluble species and living organisms, see Figure 8 [46].

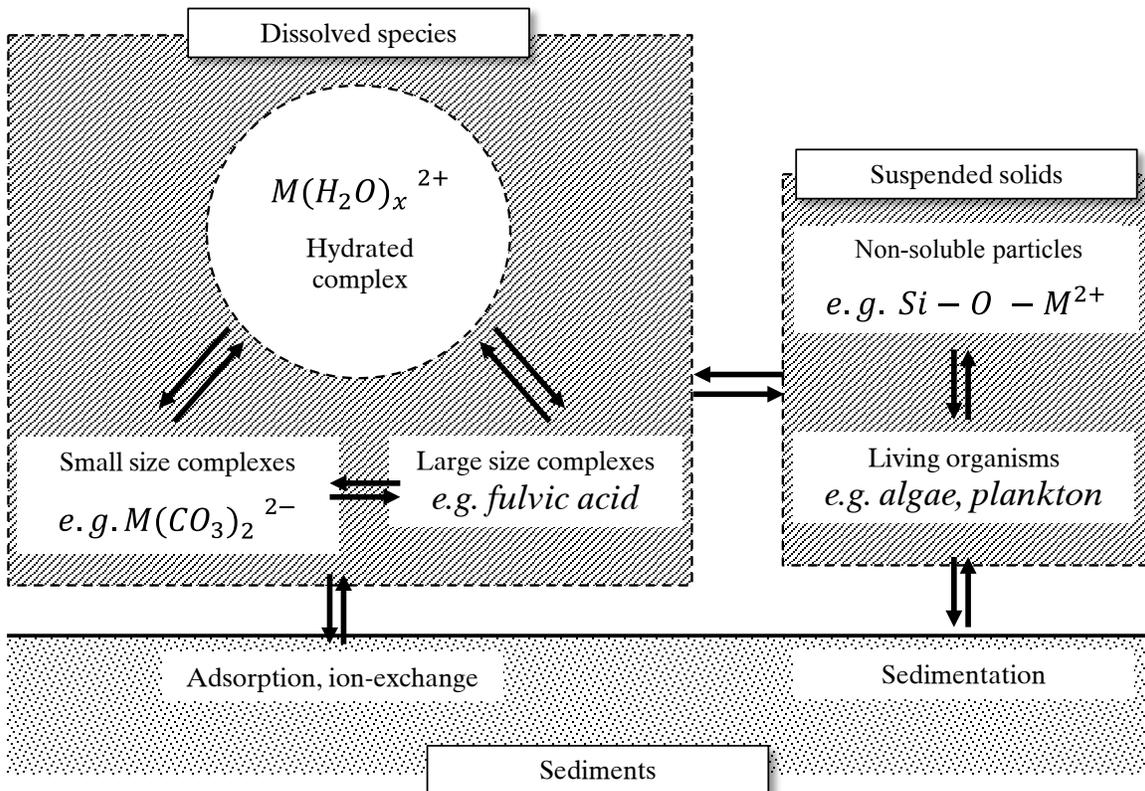


Figure 8. Schematic description of equilibrium reactions of metal species in natural water. Adapted from Buffle 1988 [46].

Due to the nature of the uptake mechanisms in aquatic organisms it is predominantly the hydrated complex form ($M(H_2O)_x^{2+}$, here M^{x+} for short) of the metal that is bioavailable, i.e. the toxicity of a metal in water closely correlates to the concentration of the free ionic form M^{x+} rather than to the total concentration of all species, M_{tot} [46, 49-52].

At a cellular level, uptake of metals in aquatic organisms is driven by a difference in chemical potential between the external medium, the cellular membrane and the intracellular medium. The net displacement of M is driven towards the medium where its

chemical potential is the lowest, or in other words, where the degree of complexation is the greatest. Furthermore, only free ionic species and complexes that meet specific criteria are available for assimilation, which is why it is mainly the activity of the free ionic species that contribute to the toxicity.

3.1.1 *Relative importance of natural ligands*

Naturally occurring ligands that may form complexes or colloids with metals, include natural organic matter (NOM), such as humic and fulvic acids, proteins and polysaccharides, and inorganic ionic species, including hydroxides, phosphates, sulphides and simple anions (PO_4^{3-} , CO_3^{2-} etc.). Of these ligands, fulvic acids (FA) are generally saturated first, followed by proteins, oxides, polysaccharides and finally simple inorganic ligands.

The order in which sites in complexing agents are saturated can be understood by considering the free energy of complex formation, expressed through the standard equation for Gibbs free energy:

$$\Delta G^\circ = -RT \ln(K) \quad \text{Equation 9}$$

where K is the equilibrium constant according to

$$K = \frac{[ML]}{[M][L]} \quad \text{Equation 10}$$

where M is the metal and L is representing any ligand complexing site. On the continuous scale of free energy, sites with the lowest ΔG° will be saturated first, i.e. strongly complexing fulvic acid sites, followed by weaker fulvic acid sites, and so on [46, 53].

The relevance of metal speciation in natural waters to passive sampling will be discussed in the following chapters.

3.2 Speciation of nitrogen and phosphorous

Species of phosphate and nitrate have a fundamental role for biological production in aquatic ecosystems. In pristine freshwater bodies phosphorus is often the limiting nutrient, and the excessive release of both phosphorus and nitrogen species from agriculture and domestic wastewater can lead to the eutrophication of lakes and watercourses [54]. The speciation of nitrogen and phosphorous compounds is of fundamental importance for their biological availability, and their speciation continuously changes due to biological activity and changes in physico-chemical properties. A simplified scheme describing the nitrogen cycle in water can be seen in Figure 9. Nitrate is an important nutrient species and is formed through nitrification of ammonia, among other formation pathways.

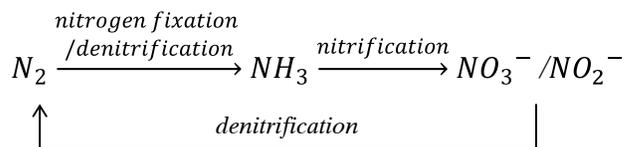


Figure 9. Simplified schematic representation of the nitrogen cycle in water.

Phosphorous is present in the water column in three main forms; orthophosphates, polyphosphates and organic phosphates. Traditionally orthophosphates have been operationally equaled to reactive phosphate (RP) or filterable reactive phosphate (FRP) commonly determined by a molybdenum blue method. However, this method has been shown to overestimate the actual concentration of orthophosphate through partial hydrolysis of other phosphate species [55].

4 Speciation with passive samplers

4.1 Metals

Determination of aqueous metal species is one of the strong points and great potential uses of passive sampling, because of its well defined and high selectivity. As models are developed and our understanding of the discrimination mechanisms improves, passive sampling devices will become important tools in ecotoxicological investigations.

Generally, free hydrated metal ions and metal complexes with sufficiently high dissociation rate are device labile and will be accumulated on the binding phase.

The technique that has the most advanced model for speciation is the DGT technology. By varying the properties of the hydrogel diffusive layer it is possible to control the selectivity. It is for example possible to decrease the hydrogel pore size by using a cross linker to discriminate against large organic complexes [56].

A number of discriminating and exclusive speciation mechanisms have been proposed to model the behavior of passive accumulation samplers [57]:

- c.1) Freely dissolved and inorganic metal species (M).
- c.2) Dissociation of labile complexes in the diffusion layer, within the timescale of diffusion across the diffusion layer (ML_1)
- c.3) Differentiation of some strongly complex bound species that upon interaction with the binding phase will form ternary ligand-metal-ligand complex (L-M-L'), effectively being device labile (ML_2).

Figure 10 schematically visualizes the model suggested by the criteria listed in item c.1-3.

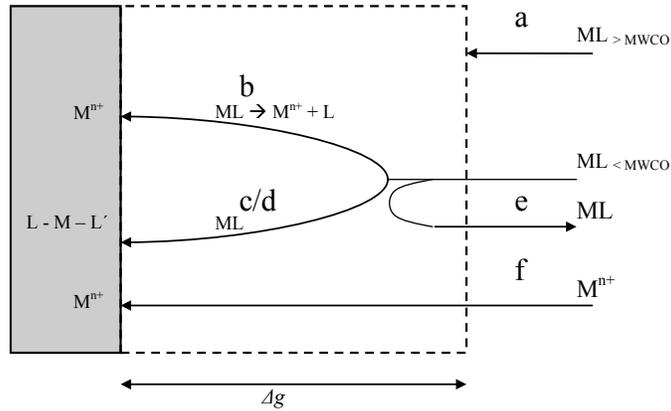


Figure 10. Schematic description of the suggested selection mechanisms. Size exclusion (a), diffusion layers dissociation (b), differentiation by the diffusion coefficients of complexes binding to the accumulating phase (c/d), exclusion of species not dissociating within the diffusion layers (e), uptake of free hydrated metal ion (f) (adapted from [58]).

The suggested model predicts the species that dissociate within the timescale of the diffusion across the diffusion layer, which can be expressed as

$$C_M = C_{ML}(1 - \exp(-k_{dis} \tau)) \quad \text{Equation 11}$$

where C_M is the concentration of free metal, C_{ML} is the concentration of the metal-ligand complex, k_{dis} is the dissociation rate constant for the ML-complex and τ is the time [59].

Considering that the time t_d that the ML-complex is resident in the diffusion layer can be described by

$$t_d = \frac{(\Delta g)^2}{2 D_{ML}} \quad \text{Equation 12}$$

where Δg (m) is the thickness of the interaction layer (diffusion layer + diffusion boundary layer) and D_{ML} ($\text{m}^2 \text{s}^{-1}$) is the diffusion coefficient of the analyte, it follows that the mass M accumulated by the device over time t can be expressed as

$$M = \frac{\left(C_{ML} D_{ML} \left(1 - \exp \left(-k_{dis} \frac{(\Delta g)^2}{2 D_{ML}} \right) \right) + C_M D_M \right)}{\frac{A t}{\Delta g}} \quad \text{Equation 13}$$

From this follows that in solutions containing both free metal species and complex forming ligand there will be one kinetic and one diffusion controlled component to the accumulation [59].

It has recently been demonstrated that the receiving phase is not a simple two-dimensional sink for the analyte, but rather act as an additional interaction volume, which means that the thickness of the receiving phase will influence the lability criteria and the lability of complexes [38, 60, 61]. While these findings do not fundamentally alter the concept of which species are available for accumulation on the passive sampler, it does widen the lability definition, allowing more species to fit the criteria.

Assuming a metal-ligand system with an excess of ligand, where the majority of the metal is present in its complex bound form, ML ($[ML]/[M_{tot}] \sim 99.9\%$), it is helpful to examine two cases:

4.1.1 Weak complexes

For weak complexes the dissociation rate constant k_{dis} is high (in this hypothetical case, $k_{dis} = 1.2 \times 10^{-2} \text{ s}^{-1}$), and thus the contribution from the ML species will dominate the analyte accumulation in a passive sampler device for most values of Δg , except for values very close to zero. The total amount of accumulated analyte M , will after an arbitrary time have a maximum for a Δg where the residence time of the complex is sufficient for it to readily dissociate. For values of Δg greater than this, the decrease in mass transport due to a longer diffusional pathway will decrease the value of M (see Figure 11).

4.1.2 Strong complexes

Strong complexes are characterized by a lower dissociation rate constant k_{dis} . For the studied hypothetical case such a complex ($k_{dis} = 3.6 \times 10^{-5} \text{ s}^{-1}$) would mean that the contribution from the free metal ion to the total accumulated mass will dominate for values of Δg up to about 0.03cm. The total accumulation M will have a maximum as Δg

approaches zero, but for increasing values of Δg over ~ 0.03 cm M will increase as the relative contribution from ML complex also increases (see Figure 11).

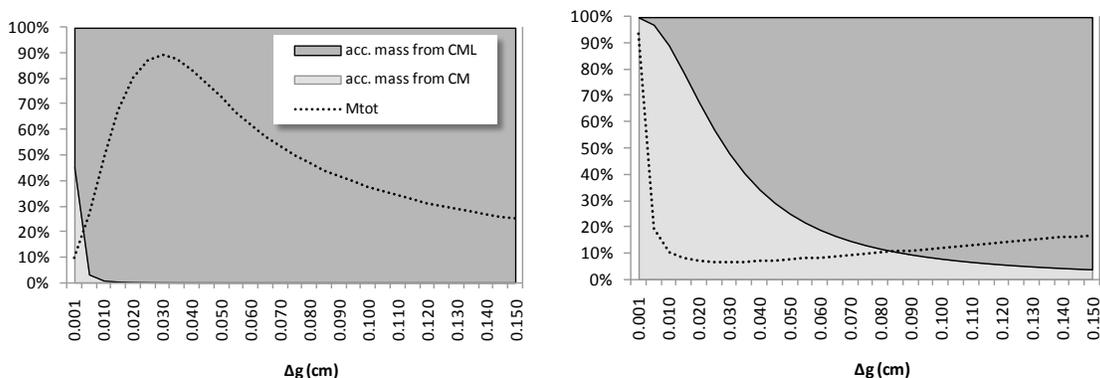


Figure 11. Charts describing the relative contribution from free metal ion (CM) and metal-ligand complex (CML) to total mass accumulation on a passive sampler for various Δg values for a weak complex (left panel) and a strong complex (right panel). The total mass accumulation is included in both panels as a dotted line (arbitrary scale).

4.2 Importance of the diffusion coefficient

There are two competing mechanisms potentially influencing the lability of a metal-ligand species. A lower diffusion coefficient (D_{ML}), which might be due to larger species or species with irregular shape, will result in slower mass transfer. On the other hand, the potential lability of the species increases, as it will remain in the diffusive layer for longer, and this increases the chance of fulfilling the second lability criteria (see c.2 above).

Similarly, increasing the diffusive layer thickness would produce the same conflicting change; decreasing mass flux because of the increased diffusion pathway, potentially increased lability of complexes according to criteria c.2 above.

By applying a similar analysis as in the previous section, using Equation 13 and studying two cases where D_{ML} is 90% and 50% of the D_M , respectively, it becomes apparent that a lower D_{ML}/D_M ratio yields lower total mass accumulation, although the value of Δg for which there is a mass accumulation maximum is also lower. In other words, larger complexes contribute less to the total accumulated mass than small complexes (assuming

the same dissociation rate), despite a potentially increased lability due to longer residence time in the diffusion layer. It should be noted that for very small values of Δg the effect of higher values of D_{ML} is negated, due to the accumulation being dominated by the free metal species (see Figure 12).

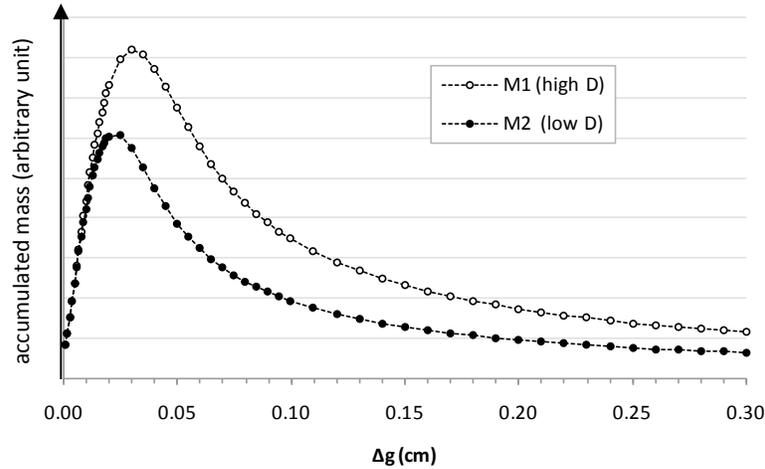


Figure 12. Chart showing the influence of the diffusion coefficient (size) for the ML complex, where D_{ML} was set to 90% (open circles) and 50% (discs) of the D_M respectively.

4.3 Confirmation of lability theory

A comprehensive numerical treatment and experimental investigation of the ligand-metal complex lability and uptake model has been described in the literature [62]. In this study the behavior of simple Cu-citrate and Cu-EDTA systems largely confirmed lability criterion (c.2) above, since the weak ($\log K = 7.2$) Cu-citrate complex was found to be fully labile, while the very strong ($\log K = 20.5$) Cu-EDTA complex was not labile [62].

Since the lability can be controlled by varying the thickness of the diffusion layer in accordance with criterion c.2 above, it should also be possible to determine dissociation kinetics by deploying two or more passive samplers with suitable diffusion layer thickness.

This means that it is possible to obtain information on the dissociation kinetics of the involved complexes by deploying devices with different diffusion layer thickness [62].

Cd and Pb in the presence of simple organic acids such as nitrilotriacetic acid (NTA) and diglycolic acid (DGA) have been shown to be mostly labile, even though the predicted degree of complexation is close to 100%. This can be explained by the fact that these relatively small complexes have diffusion coefficients that are similar to those of the free metal ion, and that they readily dissociate in the diffusion layer, and thereby become available [63, 64]

The situation in natural waters is more complicated, as the ligands are unknown, and results are difficult to interpret [65]. Organic complexation is likely to be dominated by fulvic acids (FA), and to some extent humic acids (HA) [46]. Metal-FA complexes are larger and have diffusion coefficients that are generally about 5 times lower than those of the free metal ion [65].

4.4 In situ speciation without a priori knowledge about ligands

4.4.1 Variation in porosity

As suggested above, it is not possible to know in detail what fraction is indeed sampled by the passive sampler if only one single sampler configuration is deployed. In such cases the sampled fraction must be said to be operationally defined, and consisting of freely dissolved and inorganic metal species (M), as well as metal – ligand complexes that meet the second lability criterion (ML_1) (point c.2). However, it has been suggested that by deploying two or more sets of samplers with diffusional properties that are markedly different for organic and inorganic species, a distinction between organic labile species and inorganic labile species can be made, assuming that all species within these groups can be described as having the same diffusion coefficient. According to this theory

$$M_{DGT} = M_{inorg} + M_{org} \quad \text{Equation 14}$$

where M_{DGT} is the mass of accumulated analyte on the passive sampler (DGT), M_{inorg} is the mass of accumulated analyte contributed from inorganic species and M_{org} is the mass of accumulated analyte contributed from organic species.

Applying Fick's law of diffusion we get

$$M_{inorg} = \frac{D_{inorg} C_{inorg} At}{\Delta g} \quad \text{Equation 15}$$

$$M_{org} = \frac{D_{org} C_{org} At}{\Delta g} \quad \text{Equation 16}$$

where C_{inorg} and C_{org} are the labile inorganic and organic fractions that can be measured. By combining Equation 14 - Equation 16 we get

$$M_{DGT} = \frac{(D_{inorg} C_{inorg} + D_{org} C_{org}) At}{\Delta g} \quad \text{Equation 17}$$

Since $At/\Delta g$ is constant for a given exposure, Equation 16 can be simplified and rearranged to

$$\frac{M_{DGT}}{K D_{inorg}} = C_{inorg} + \frac{D_{org}}{D_{inorg}} C_{org} \quad \text{Equation 18}$$

The right side of the equation has the form of a straight linear equation with the concentration of the inorganic labile fraction as the intercept and the concentration of the organic fraction being the slope. It is clear that to get at least two points on the line and determine the concentration of the inorganic and organic fractions it is necessary to choose passive sampler configurations so that the ratio D_{org} / D_{inorg} is different [65, 66], e.g. by using different gel compositions.

4.4.2 Different receiving phases

Lability criteria may be defined according to metal complex-binding phase interaction (see criteria c.3). It can then be assumed that if the stability constant of the metal - binding phase (MB) is significantly larger than that of the metal - ligand complex (ML), *and* if the binding phase interacts with the ML, then a ligand substitution reaction can occur [58].

In effect this mean that the method proposed in the previous section is not sufficient to fully characterize the labile fraction, and that another approach is needed.

By changing the binding phase, the stability constant of the MB complex can be altered, as well as the binding phase – ML interaction mechanism, thus enabling the deployment of passive samplers to investigate this mechanism.

It was found that in ‘simple’ synthetic solutions in the presence of ligands (EDTA and humic acid) under laboratory conditions, the different configurations of DGT devices essentially measured the ‘free’ fraction of metal ions. However, in a field deployment experiment in natural water it was statistically shown that the different binding phases yielded different derived concentrations of metal. These results were in good agreement with the binding strength theory [58].

4.4.3 Comparison with computer speciation codes

It is possible to estimate metal speciation using computer simulation codes, such as MINTEQ and WHAM, to calculate equilibrium concentrations of different species based on known complex formation constants and other physical factors [67, 68]. Results from such calculations may be reinforced or contradicted by measurements using passive samplers. Generally, there is a good agreement between computer model output and passive samplers when comparing results in simple systems in laboratory environment [64, 69], while field applications in complex environment often show discrepancies to a varying extent [70], something which is also described in Paper V. Figure 13 shows the results from a measurement using passive samplers in a urban runoff sedimentation chamber where the modeling output partly agrees with the results obtained with a passive sampler. By adjusting the input characteristics of the fulvic to humic acid ratio of the dissolved organic matter (DOM) in the speciation model used (visualMINTEQ) it was possible to improve the level of agreement to some extent, but the main conclusion was that the passive sampler labile fraction is not restricted to the strictly dissolved fraction, but, as described by the lability criteria (c.1-3), parts of the metal-ligand species will also be labile under certain conditions (see previous discussion in this section).

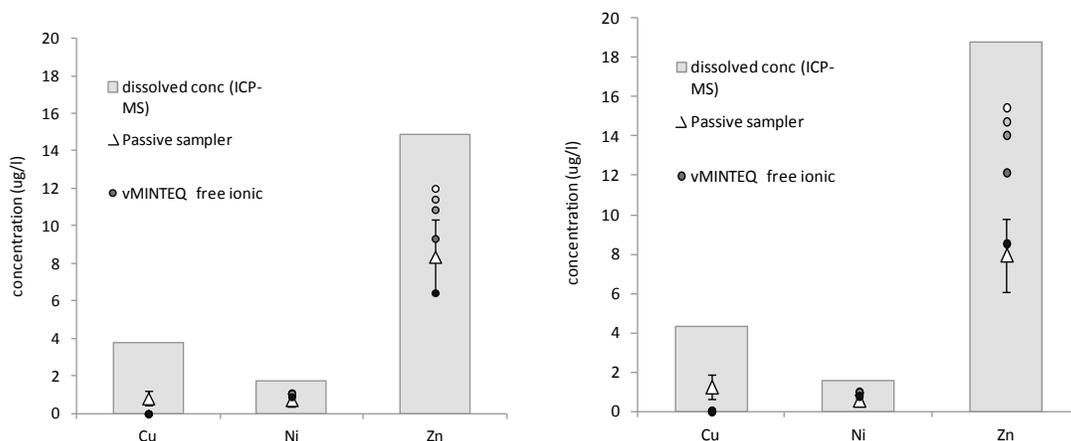


Figure 13. Concentration results for the 7 day (left) and 14 day deployments (right) of passive samplers (Δ) compared with the total dissolved concentration from pooled samples (bars) and speciation code predictions for FA:HA ratios, ranging from 1 (\circ) to 0.4 (\bullet). Paper V.

It is also suggested that it is unlikely that a full agreement between equilibrium speciation calculations and passive sampler measurement results in a dynamic, non-equilibrium, system can be achieved, as the passive sampler measurement responds to dynamic changes as opposed to equilibrium models.

4.5 Relevance to toxicity assessment

One of the most promising applications for passive sampling devices is as a substitute or complementary method to bio assays or toxicity screening tests. Several studies have looked at the correlation between passive sampler results and observed biological response [45, 71, 72].

A comparison between passive samplers (DGT) and *Daphnia magna* acute toxicity test in wastewater media for Cu and Cd [73] and for Cu in mineral water spiked with various organic ligands has shown that the passive sampler results were in good agreement with half maximal effective concentration (EC_{50}) values. These results may be more difficult to interpret if the organic complexing compounds present are of mostly non-humic nature, as under such conditions the passive sampler overestimates the bioavailable Cu fraction [50].

Furthermore it has been shown that passive sampler labile Al and Cu fractions adequately predict the stress response [74] and gill concentrations of Cu [75], further indicating the applicability of passive sampling for purposes of estimating bioavailable fractions.

Given the integrative nature of the passive sampling technology and the demonstrated inherent selectivity towards the bioavailable metal fraction there is a strong case for using passive samplers to provide additional links to the evidence chain in ecological risk assessments.

4.6 Nitrate and phosphate

The research literature concerning the passive sampling of nutrients is relatively limited, and most of the existing publications primarily address phosphate [19, 21] although a novel passive sampler was recently applied to both NO_3^- and P [22]. The most common receiving phases are based on ferrihydrite [76-78], but zirconium oxide [79] and titanium dioxide [19] have also been used.

The available literature on phosphate speciation suggests that the passive sample available species are approximately equal to the reactive phosphate fraction [21, 79, 80]. In cases where ferrihydrite or zirconium oxide based receiving gel was used, little effect was seen from changes in pH ranging from 1 to 9, indicating that these binding agents have affinity towards H_2PO_4^- , HPO_4^{2-} as well as PO_4^{3-} . In contrast, passive samplers fitted with an anion exchange resin as a receiving phase showed strong dependence on the pH of the solution, suggesting a selectivity towards HPO_4^{2-} (see Figure 14 and Paper VI).

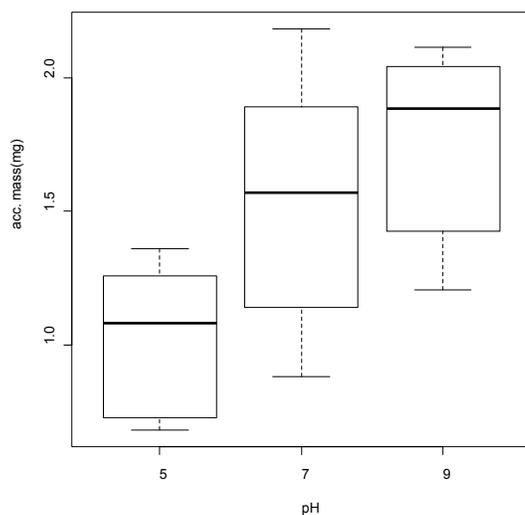


Figure 14. Box and whiskers plot showing accumulated amounts of phosphorous and variance from pH in a multifactorial experimental design. The effect of the pH on the amount accumulated was different from random variation, $p < 0.01$ (from Paper VI).

Very little has been published about nitrogen speciation on passive samplers. A passive sampler (SorbiCell) was applied for the determination of nitrate in catchment streams and showed good agreement with both continuous probe and grab sampling measurements of NO_3^- [22].

The passive sampler described in Paper VI showed good agreement between the concentration of NO_3^- and HPO_4^{2-} derived with the passive sampler, and concentrations determined using ion chromatography in effluent water from a wastewater treatment plant (see Figure 15).

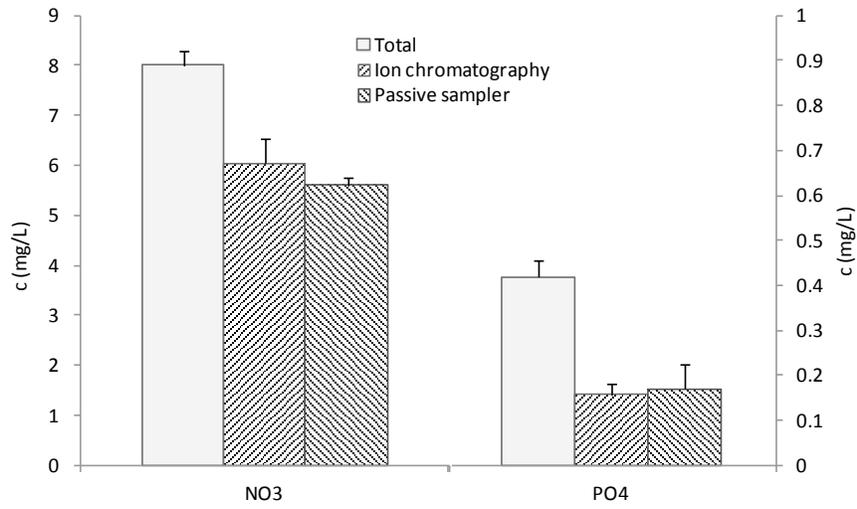


Figure 15. Concentration of total, ion chromatography and passive sampler derived results for nitrate/nitrogen and phosphate/phosphorous respectively. The N-species values are shown on the left axis while the P-species are shown on the right axis (from Paper VI).

5 Experimental

5.1 Experimental procedure of the passive samplers

In this section follows a detailed description of the preparation and extraction of the passive samplers used in the experimental work of this thesis.

5.1.1 Chemcatcher®

The Chemcatcher was prepared by acid washing of sampler housing using 1M HNO₃, and subsequently rinsing in deionized water. The receiving phase consisted of Empore™ Chelating Disk and was conditioned by washing the disk in a vacuum filtration equipment using 50 mL deionized water, 40 mL 1M HNO₃, followed by a rinse using 40 mL deionized water. The disk was then activated by applying 50 mL 3M ammonium acetate and finally rinsed using 40 mL deionized water. The diffusion limiting layer consisted of a Sartorius cellulose acetate filter (nominal pore size 0.45 μm) that was soaked in deionized water overnight.

After the preparation procedures the device was assembled and stored in deionized water until used.

Extraction after exposure was conducted in vacuum filtration equipment, where the receiving phase disk was extracted using 40 mL 1M HNO₃. The extract was collected and diluted 1:10 prior to analysis.

5.1.2 DGT

For the purpose of the experiments described in the appended papers I-III, DGT passive samplers (DGT Research Lancaster, UK) were used.

Extraction after exposure were done by opening the sampler and transferring the receiving phase resin gel to a test tube, adding 2 mL 1M HNO₃ and leaving it for 24 hours. The eluate was then diluted 1:5 prior to analysis.

5.1.3 Procedural and field blanks

As a quality control measure procedural and field blanks were used. Procedural blank passive samplers were prepared and treated as described above, but were not brought to the field. Field blanks were brought to and opened in the field at the sampling location. Blank samplers were extracted and analyzed in the same way as ordinary samplers.

The results from the blanks were used when calculating TWA values as described previously. No statistically significant difference between procedural and field blank passive sampler results was observed.

All preparation and extraction handling were done using equipment that had been thoroughly cleaned, acid washed and rinsed in laboratory grad deionized water.

5.2 Laboratory calibration

During development of the Chemcatcher® passive sampler, calibration experiments were conducted in the laboratory in order to derive sampling rates for the studied metals (Cu, Cd, Cu, Ni and Pb) and for different environmental settings. To achieve a controlled environment the prepared passive samplers were attached to a turntable (see Figure 16). The turntable was placed in a barrel tank (approx. 50 liter volume), which in turn was placed in a large external tank (approx. 300 liter). The external tank was filled with a water – glycol mix. An immersion cooler was used in conjunction with a thermo regulated immersion heater to keep the temperature stable at the desired level (7, 14 or 21 °C). The exposure tank was filled with a solution consisting of metal ions at a nominal concentration of 10 µg L⁻¹. The ionic strength was regulated by adding 10mM NaNO₃ and pH was adjusted to 6.5-7.0 using dilute NaOH.

At the beginning of the exposure the prepared passive samplers (16 samplers per calibration) were attached to the turntable and immersed in the exposure tank. The

turntable was then attached to an overhead stirring motor, which was adjusted to keep the turntable rotating at 40 or 70 rpm respectively.

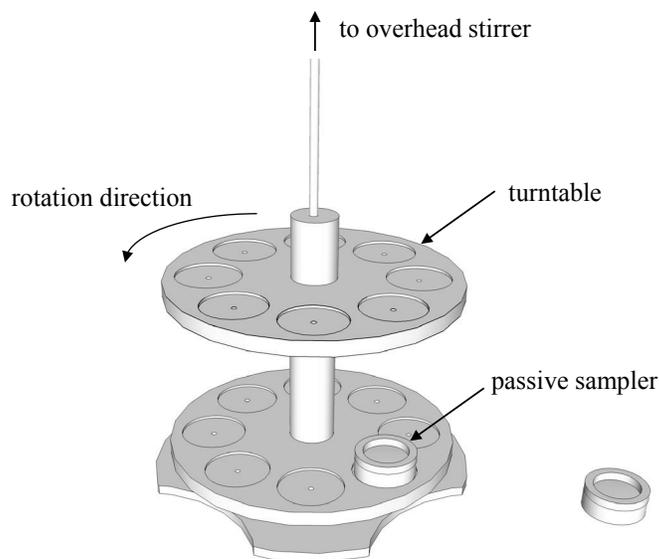


Figure 16. Schematic view of the turntable used during calibration experiments of Chemcatcher® passive samplers.

The solution in the exposure tank was continuously replenished from a fresh stock solution with the same composition as described, at a rate of 25 liters per day. Samplers were removed from the turntable daily and extracted in accordance with the procedure described above. All equipment in contact with the solution in the exposure tank was acid washed and thoroughly rinsed with deionized water before use.

5.3 Field exposures

Measurement with passive samplers in the field often requires ad-hoc solutions depending on sampling location. If the area is accessible to the public it can often be desirable to hide the sampling equipment or place it out of reach, to minimize the risk of accidental or intentional interference from by-passers. If the sampling location is in a restricted access area such precautions are not necessary. During field exposures in papers V and VI the passive samplers were attached to a simple sheet of polyacrylate plastic using cable ties. In the storm water treatment facility (Paper V) the water level could vary with several meters, so the passive samplers needed to be fixed. The fixture

was attached to two buoys (see Figure 17) to keep the passive samplers at a constant level below the surface. In the field exposures for Paper VI the sampling were carried out in a restricted area in a process tank, so the sampling fixture could simply be attached to the existing structure using cable ties.

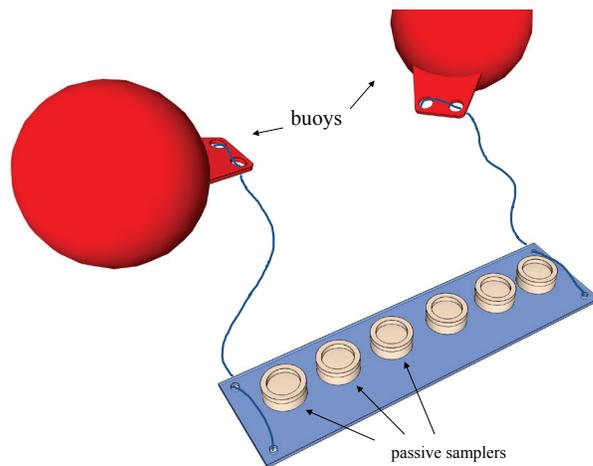


Figure 17. Schematic drawing showing a fixture for passive samplers, attached to floating buoys for field exposure.

5.4 ICP-MS

Inductively coupled plasma–mass spectrometry (ICP-MS) is a powerful analytical technique for determination of over 80 different elements at concentrations down to sub-ppb, or even sub-ppt ($<10^{-12}$) levels depending on the element and the sample matrix. For the analytical work described in this thesis a Perkin-Elmer ELAN 6000 instrument was used.

The ICP-MS analysis generally requires a liquid sample, which is turned into a fine mist of aerosol droplets in a nebulizer inside a spray chamber. In the spray chamber larger aerosol drops are separated and led to waste. Only the finest fraction of aerosol drops are transferred by a carrier gas (commonly Argon) from the spray chamber into the plasma region of the instrument.

The plasma in the ICP-MS is maintained by electromagnetic induction which raises the temperature of the feed gas (Argon) to roughly 6000 K, at which point plasma is formed.

As the sample aerosol drops enters the plasma region the constituents are atomized and ionized, i.e. molecules are broken into their atomic parts and due to the high temperature the atoms form positive ions, M^+ (see Figure 18).

After the ionization in the plasma, the sample pass through a series of 2-3 small openings (cones) which serve as an interface between the atmospheric pressure in the torch box and the high vacuum ($<10^{-5}$ torr) in the mass spectrometry compartment of the instrument.

In the mass spectrometer the ions formed in the plasma are accelerated through a quadrupole, where ions are separated in a variable electric field, based on their mass to charge ratio (m/z). Only one mass to charge fraction is permitted to reach the detectors at any given moment. This allows the element to be quantified through counting the ions hitting the detector. By scanning over the mass to charge spectrum a large number of elements can be detected and quantified.

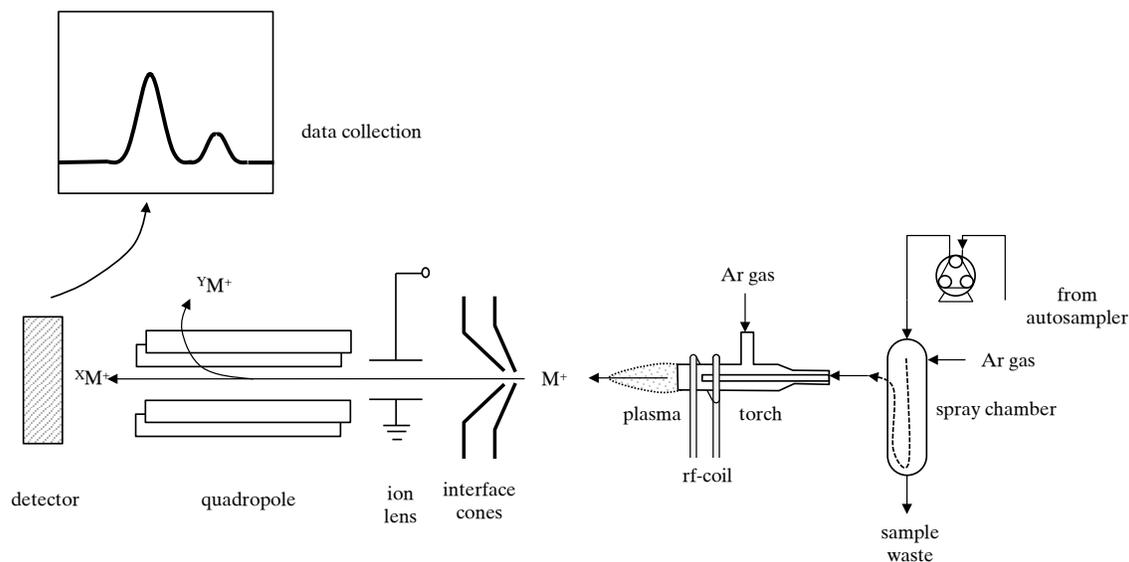


Figure 18. Schematic drawing of the principal components of an ICP-MS instrument (based on the Perkin-Elmer ELAN 6000).

5.4.1 Interferences

Although analysis using ICP-MS is usually reliable and accurate, it is important to be aware of some common types of interferences described below.

5.4.1.1 *Isobaric overlap*

A majority of the elements in the periodic table has two or more isotopes, e.g. ^{63}Cu and ^{65}Cu , or ^{54}Fe , ^{56}Fe , ^{57}Fe and ^{58}Fe . In some cases isotope mass overlap, as in the case with for example ^{58}Fe and ^{58}Ni , and ^{114}Sn and ^{114}Cd . The mass of these isotopes are not exactly the same, but the resolution of the mass spectrometer may not be good enough to distinguish between $^{58}\text{Fe}^+$ and $^{58}\text{Ni}^+$, and thus the signal at this m/z ratio will be a combination of Fe and Ni ions.

However, as natural isotope ratios are well known and constant for the vast majority of elements, isobaric overlap can be corrected mathematically. This mathematic correction is usually done automatically by the instrument acquisition software.

5.4.1.2 *Doubly charged ions*

In the plasma a small fraction of the atoms are excited into doubly charged ions, i.e. M^{++} . As the doubly charged ions enter the mass spectrometer they may interfere with single charged ions at half the mass. For example $^{120}\text{Sn}^{++}$ will have a similar m/z ratio as $^{60}\text{Ni}^+$, thus Sn will contribute to the $^{60}\text{Ni}^+$ signal. This will lead to erroneously high reported concentration for Ni and thus an artifact that have to be taken into consideration. The common strategy to minimize interference from doubly charged ions is to minimize the formation in the plasma through instrument optimization.

5.4.1.3 *Polyatomic interferences*

In the outer plasma regions the temperature is lower, which allows the formation of polyatomic species, such as oxides, chlorides and argon species. The presence of polyatomic species leads to potential interference problems. Considering for example the following pairs it becomes apparent that this type of interference is potentially problematic: $^{40}\text{Ar}^{16}\text{O} - ^{56}\text{Fe}$, $^{40}\text{Ar}^{35}\text{Cl} - ^{75}\text{As}$, $^{23}\text{Na}^{16}\text{O} - ^{39}\text{K}$ and $^{23}\text{N}^{16}\text{O} - ^{39}\text{K}$. Thus the determination of As^+ in samples containing chloride is prevented by the formation of ArCl^+ (both species have the m/z ratio 75, $\Delta m = 0.00963$ g).

Possible workarounds include the use of high resolution ICP-MS instruments that can resolve very small differences in mass, or using reaction gas cell to convert the analyte to

a species where there is no interference from other species, e.g. oxygen can be used in the reaction cell to convert $\text{As}^+ \rightarrow \text{AsO}^+$ ($m/z = 91$).

5.4.2 Instrument optimization

The ICP-MS instruments performance is optimized daily to ensure that the minimum performance criteria are met. Oxide levels and doubly charged ions were at all times below 3% and the background signal at $m/z = 220$ were below 5 counts per second. After optimization the instrument gave at least 300k counts per second for a 10 ppb Indium solution and the relative standard deviation was better than 1%.

5.4.3 Calibration

The ICP-MS was calibrated using commercially available multi element standard solutions (Merck, Sweden). Calibration standards were prepared in dilution series ranging from 1 to 5000 $\mu\text{g L}^{-1}$. It was ensured that the correlation coefficient of the calibration curves were always >0.999 for the elements of interest.

6 Quality of passive sampler measurements

The passive sampling technique is associated with a number of potentially problematic characteristics; the most challenging is the fact that the analyst has no control over and/or knowledge about the sampling situation when the device is deployed in a water body. Environmental factors, such as temperature, turbulence and bio fouling, will all influence the rate of uptake of the analyte on the passive sampler [81] (Paper III), adding uncertainty to the determination of the time weighted average concentration. The relative impact of these factors varies from device to device. For example, the Chemcatcher[®] is relatively sensitive to changes in turbulence as a result of its thin diffusion limiting membrane, while the thicker hydro-gel used in the DGT makes that device less sensitive.

In general, the deployment and analysis of passive sampler devices follows the procedure *preparation, deployment/exposure, extraction and quantification*, together with necessary handling of the device in all the steps mentioned. This sequence is usually followed by a calculation where previously established calibration data is used to correlate the accumulated analyte to a water column concentration. All these operations introduce uncertainties and possible errors, some of which can be alleviated by employing fabrication and field blanks to assess contamination, and by spiking the device during preparation to determine analyte recovery (see Figure 19). The quantification of the accumulated analyte should follow normal analytical procedures to ensure data quality.

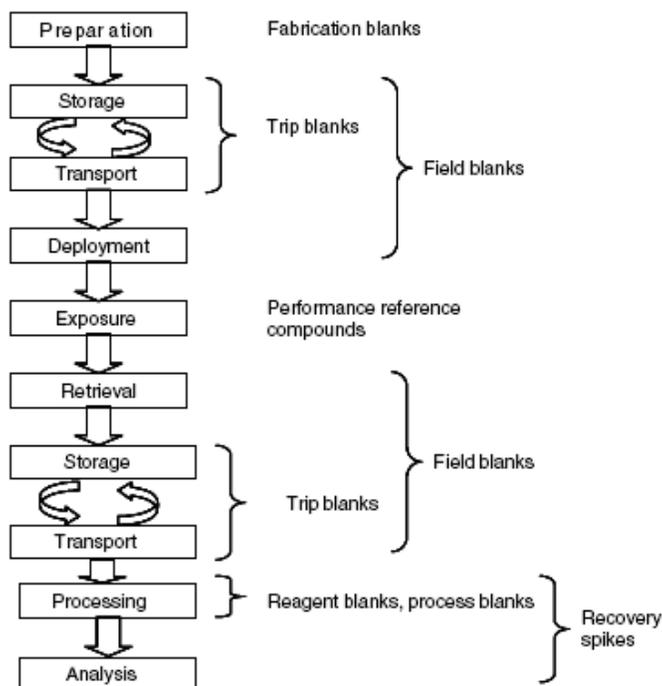


Figure 19. Schematic description of passive sampler procedure with suggested quality control checks (from Paper IV).

From the extraction step on it is possible to employ a prepared reference material (in instances where this is available) to control the extraction and quantification and to follow ordinary quality control procedures. Other potential sources of error such as contamination and poor recovery are easier to address and minimize by adhering to strict standardized procedures, and are not considered as major obstacles to implementation in regulatory monitoring. This is also supported by findings presented in Paper VII.

6.1 Diffusion coefficients

Diffusion coefficients of metal ions for DGT have been widely studied and reported [56, 82, 83]. The same is true for complexes of metals with humic and fulvic substances [82]. Diffusion coefficients have also been reported as dependent on the ionic strength in cases of solutes immersed at low ionic strength of the immersion solution [40, 84] and there is data on the most commonly used reference materials of humic substances and on metal complexes with small organic molecules, such as nitriloacetic acid and diglycolic acid. Corresponding data (sampling rates) for the Chemcatcher[®] passive sampler have been published for certain metals [8, 32, 85](Paper V) and anionic species (Paper VI).

6.2 Environmental factors

6.2.1 *The use of performance reference compounds*

Researchers have used performance reference compounds (PRC) to account for environmental variability and its effect on accumulation rates. The theory postulates that offloading kinetics are governed by the same mass transfer law as uptake kinetics. In the case where the bulk water concentration of the PRC is zero, this can be described by the equation

$$m_D(t) = m_D(0) \exp(-k_e t) \quad \text{Equation 19}$$

where m_D is the mass of the compound on the receiving phase at time t , $m_D(0)$ is the mass of the compound at $t = 0$ and k_e is the rate constant.

Such PRCs have been successfully used together with non-polar samplers and it has been demonstrated that a good correlation between variations in uptake and offloading kinetics can be achieved under a broad range of environmental conditions [33], indicating isotropic exchange kinetics.

For polar samplers where the analyte retention to the receiving phase is stronger or where the exchange kinetics are anisotropic, the application of PRC:s is not as straightforward [24, 33, 86], and for metals such a PRC has yet to be demonstrated.

Recently, however, a way of compensating for the local flow regime was shown using gypsum cast in plastic tubes. The mass loss of gypsum was found to be proportional to the surrounding flow rate and the information derived from the gypsum device was successfully used to correct the results from passive sampler measurement of phosphate [35, 87].

6.2.2 *Conservative elements*

Other possible ways to address quality control in the accumulation step could involve so-called conservative elements that could potentially be employed as external standards and used to compensate for deviations in the accumulation caused by environmental factors.

The challenge in passive sampling quality control concerns mainly the accumulation step, where in an in situ sampling situation there is no control over factors that may influence the accumulation rate. Some factors can be monitored and compensated for relatively easily (e.g. temperature), while others are more difficult to assess (e.g. bio fouling, sediment fouling and turbulence).

6.3 Reproducibility

The relative standard deviations for time weighted average (TWA) concentration determination using passive samplers vary depending on the device, analyte and sampling situation. Recent studies with replicate samples have shown RSD values ranging from 1.0 to 11.8% in a controlled environment exposure (Paper II) up to as high as 71% for Pb during field exposures of the DGT [88], even though the observed reproducibility (RSD) is generally within the 10% range for field deployments [10, 65, 69, 89].

6.4 Robustness

The robustness of a method denotes its repeatability over time, as well as its repeatability with different operators, equipment and laboratories. A robust method should yield consistent results even if the above mentioned factors are changed, and this is also an important requirement in the WFD [90] (Paper I) .

According to a set procedure, where five samplers were exposed to artificial solutions containing Cd^{2+} and Cu^{2+} at $100 \mu\text{g l}^{-1}$ nominal concentration for seven days, under controlled turbulence and temperature conditions. This exposure was repeated a second time. The samplers were then extracted at the laboratory performing the exposure, and sent to a coordinating laboratory, where the final determination was done using ICP-MS.

The results from this inter laboratory calibration trial showed a large variation in the results with a RSD value of 21.7 and 22.8% for Cd and Cu respectively (see Figure 20 and Table 3, unpublished data of the author). This indicates that some aspect of the method is not giving the intended results, and that the method should therefore be revised and improved on until a more consistent performance is achieved.

Table 3. Summary of the round robin trial for inter laboratory comparison showing the average passive sampler derived concentration, standard deviation and relative standard deviation for Cd (n=70) and Cu (n=80) in test solution and blank samples (n=40) respectively.

	Cd ($\mu\text{g l}^{-1}$)	Cu ($\mu\text{g l}^{-1}$)	Cd blank ($\mu\text{g l}^{-1}$)	Cu blank ($\mu\text{g l}^{-1}$)
Average \pm 95% confidence interval	66.2 \pm 3.4	55.1 \pm 3.2	0.1 \pm 0.2	0.8 \pm 0.3
Standard deviation	14.4	12.8	0.3	1.0
RSD (CV%)	21.7%	22.8%	259%	133%

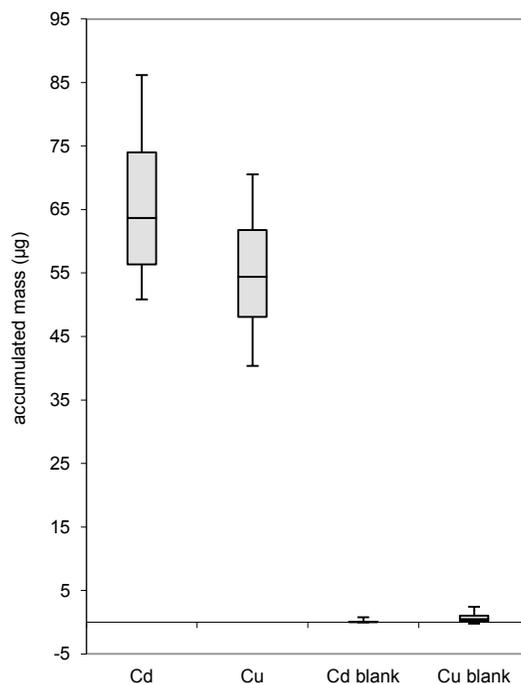


Figure 20. Accumulated mass of Cd and Cu on a passive sampler during a 7 days exposure in an inter laboratory calibration trial. Samplers were exposed to artificial solutions with nominal concentration of 100 $\mu\text{g l}^{-1}$ for Cd (n=70) and Cu (n=80) respectively. Blank exposures were performed as well (n=40). Eight laboratories participated in the trial.

6.5 Field validation

An important tool for assessing the quality of passive sampling determinations is field validation where concentrations obtained using passive samplers are compared to those obtained with conventional sampling techniques in order to validate the method for *in situ* experiments. Interpretation of such trials is not straightforward as the mode of sampling achieved with passive sampler *in situ* measurements does not directly correspond to traditional grab sampling, as previously discussed [3].

A field validation trial was performed where passive samplers were exposed in a semi-controlled environment, where fresh river water was supplied to a tank, in which passive samplers were exposed, and compared with the results from frequent grab sampling (see Figure 21).

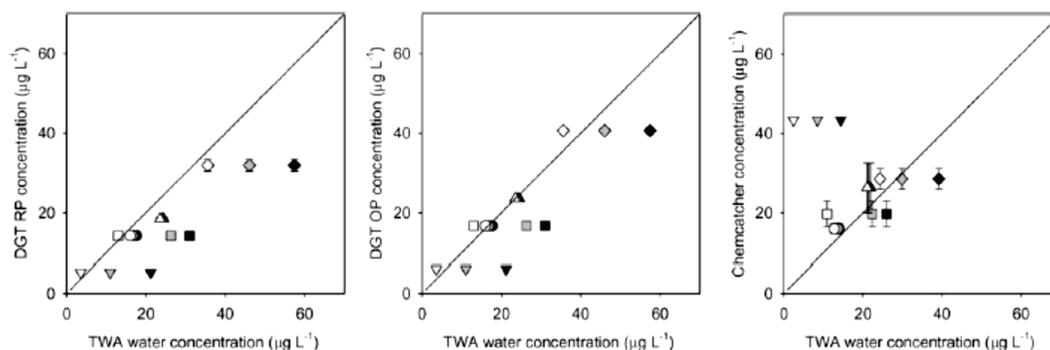


Figure 21. Comparison of TWA concentrations measured by DGT with OP and RP gels and Chemcatcher® with total (black symbol), 0.45 mm-filtered (grey symbol) and 5 kDa-filtered concentrations (white symbol) for Cd (○), Cu (□), Ni (△), Pb (▽) and Zn (◇). Note: standard deviations of DGT are smaller than the size of the symbol unless otherwise shown. For the Chemcatcher®, error bars represent the range of TWA metal concentrations based on the 2 possible uptake rates (based on calibration data at 18 °C and $v = 40$ or 70 cm s^{-1} , respectively) (Paper II).

Another relevant comparison is made with analogous *in situ* techniques, such as Gel-Incorporated Micro Electrodes (GIME) which can also be used for [91]. Such comparisons have been made for several field deployments [69, 92] and the result for the passive samplers and GIME were in approximate agreement for Pb and Cd, while for Cu the DGT reported significantly higher values than the GIME. This is not unexpected as

the labile fraction should be lower for the GIME due to the shorter timescale of measurement [93].

Zhang et al (2004) reported on a comparison of the time-averaged results for total dissolved metals determined by ICP-MS, Anodic Stripping Voltammetry (ASV) and DGT. As expected due to the more generous lability criteria it was found that ASV yielded values between those of total dissolved and DGT [65].

A comparison between DGT, dialysis samplers and results from on-site filtration in five lakes for Cu, Zn, Fe and Mn revealed good agreement between all three techniques for acidic oligotrophic lakes where the most abundant species were likely to be simple inorganic complexes and freely dissolved ions. However, in a circumneutral lake where higher levels of humic and fulvic acids were present, complexation of some metals led to large discrepancies and the DGT yielded lower results than the other methods [10].

Ultrafiltration was compared to the results from DGT samplers in brackish waters by Forsberg et al (2006) [94]. The outcome of this comparison was ambiguous, as the level of agreement varied between metals, but also between sampling sites, probably reflecting differences in metal speciation, causing the difference in lability criteria/exclusion mechanism between the two sampling approaches to become acutely significant.

The overall conclusion from these studies must be that due to the complex and highly specific mechanisms that govern accumulation of analyte on passive sampler, a conclusive field validation is difficult to achieve. It could therefore be said that the accumulation stage of the passive sampler is operationally defined, while the subsequent laboratory procedure with extraction and analysis is a conventional procedure.

6.6 Uncertainty analysis

Uncertainty analysis can be used to assess method performance and identify problematic areas [95] where method uncertainty can effectively be reduced. In order to identify sources of uncertainty it is useful to construct a cause-effect graph which visualize the method [96], see Figure 22.

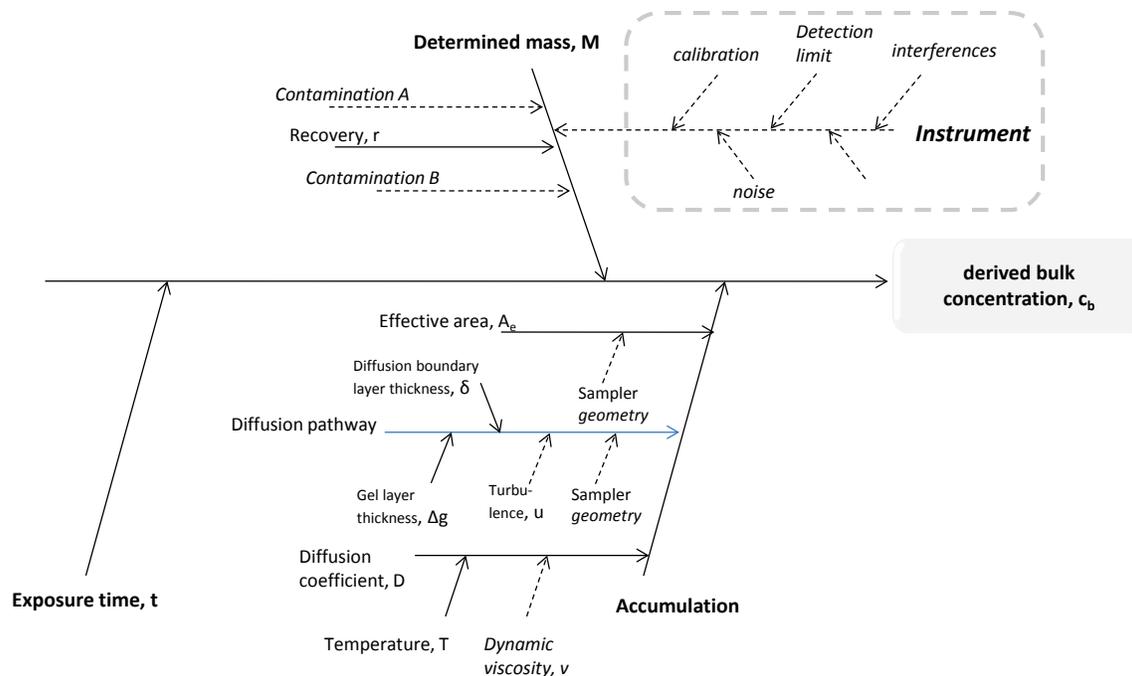


Figure 22. Cause-effect graph showing potential sources of uncertainties in passive sampler measurement (Paper VII).

In Paper VII an uncertainty budget for a passive sampler was estimated and it was concluded that the largest source of uncertainty was the determination of the effective area of the opening through which diffusion occurs. The main reason for the uncertainty comes from the lateral diffusion around the edges of the sampler opening which results in an effective sampling area, A_e , that is larger than the nominal geometric area of the sampler body [44]. This effect has been reported for the DGT type passive sampler, but the effect of lateral diffusion at edges is probably influencing all passive samplers of similar design, e.g. the Chemcatcher[®]. Second most important are the analytical steps, including preparation, extraction and instrumental determination of the analyte(s) which introduces a large number of potential sources for uncertainty, and whose pooled contribution to the total uncertainty can be seen in Figure 23.

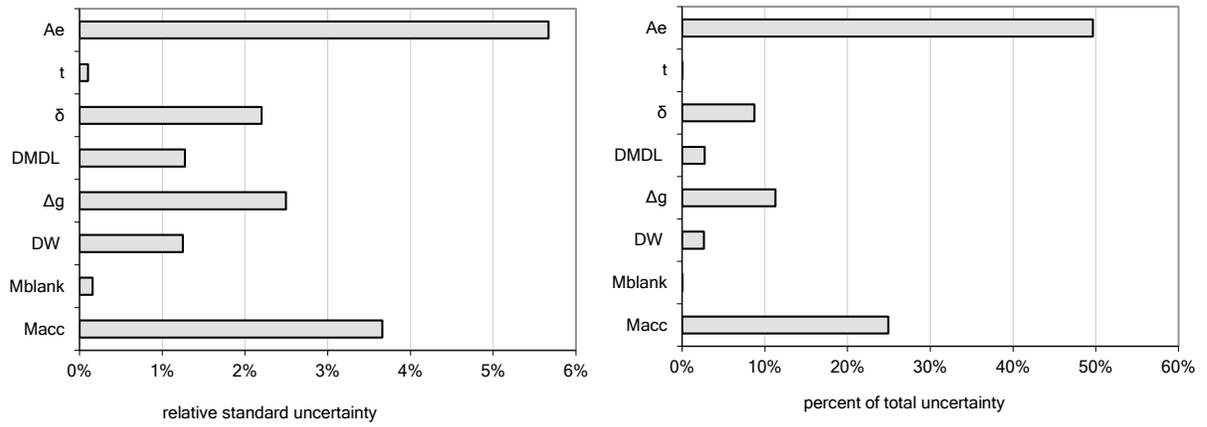


Figure 23. Relative standard uncertainty (left) and the percentage of total uncertainty (right) for the variables in the model equation (Paper VII). A_e = effective area, t = time, δ = DBL, DMDL = diffusion coefficient of the analyte in the DML, Δg = DML thickness, DW = diffusion coefficient in water, M_{blank} = determined mass in blank sample and M_{acc} = determined accumulated mass of sample.

7 Concluding remarks

For new monitoring techniques to find their way into monitoring programs a number of key requirements must be met; they must be cost-effective, reliable and representative [45], meaning that measurements have to be comparable on an international level, and they must provide representative values even in circumstances where concentrations may fluctuate (Paper III).

7.1 Passive sampling in WFD

The WFD is based on risk assessment procedure, where it is of great importance to reduce the level of risk in decision making (see Figure 24). Therefore the clearly stated objectives for the water monitoring are defined as the use of proper monitoring tools that can provide information with good precision and high confidence.

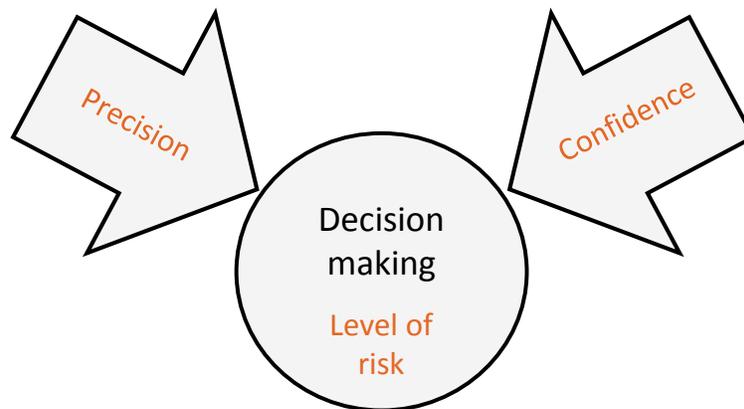


Figure 24. The relation between precision, confidence and risk in decision making.

The WFD emphasizes a holistic perspective on monitoring and ecological assessment [97]. Based on the demonstrated performance of passive sampling devices in the present work, it is therefore likely that this form of monitoring will emerge as a method that can

link anthropogenic stressors (metals) to ecological response in a more straightforward way than discrete grab sampling is able to do.

Two main reasons for this have been presented in this thesis: a) the integrative sampling of pollutant and b) the selectivity, both of which are analogous to the uptake in organisms, and also mimic the ecotoxicological effect better than the static speciation models [98] and the traditional grab sampling.

7.1.1 Integrative sampling

Passive sampler devices react to fluctuations in analyte concentration. This was demonstrated in a tank experiment where passive samplers were exposed to river water to artificial peaks in metal concentration, through spiking (see Figure 25) and to storm water drainage facility. Passive samplers appeared to respond to fluctuating concentrations, providing TWA pollution loads (see Figure 26) that were in good agreement with the ones obtained through frequent grab sampling. Passive samplers could therefore be useful in investigative monitoring in combination with grab sampling to help identify trends in water bodies with fluctuating analyte levels [6, 99] (Paper I and III).

7.1.2 Selectivity

Passive sampling devices show selectivity to the device-labile pollutant fraction. This was demonstrated through direct comparison with frequent grab sampling of total and filtered concentration. Additional speciation assessment was done through computer speciation modeling performed on natural waters. The selectivity of the passive sampling device was shown to be closely related to the bioavailable fraction of the pollutants and thereby to its ecotoxicological effect (e.g. Figure 13). This is in agreement with the indicator based approach suggested in WFD guidance document 7 [100].

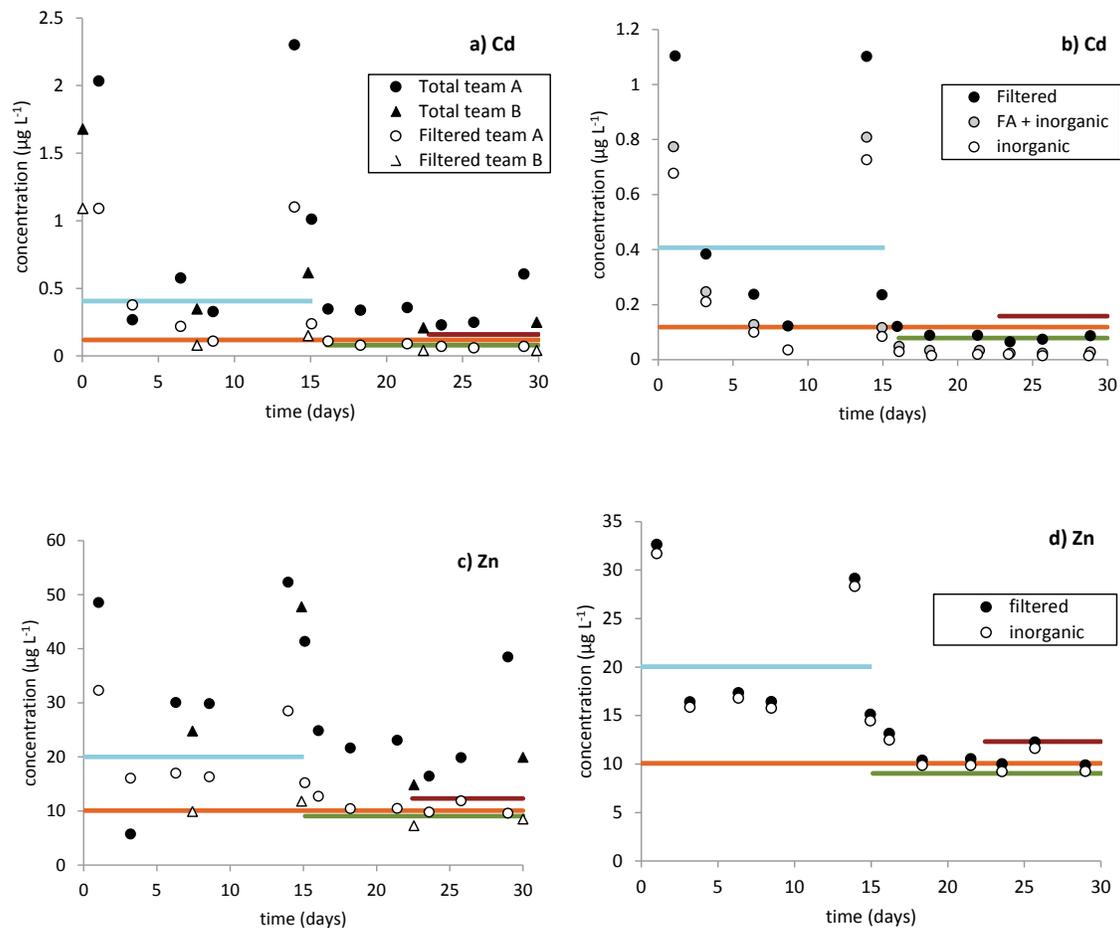


Figure 25. Comparison of the results for total (● and ▲) and filtered (○ and △) metal concentrations (a, c, and filtered (●), FA + inorganic (○) and inorganic (○) fractions respectively (b, d) determined by grab sampling and metal concentrations determined by 7, 14 and 21 day deployments of DGT passive sampling devices (solid colored lines) (from Paper III).

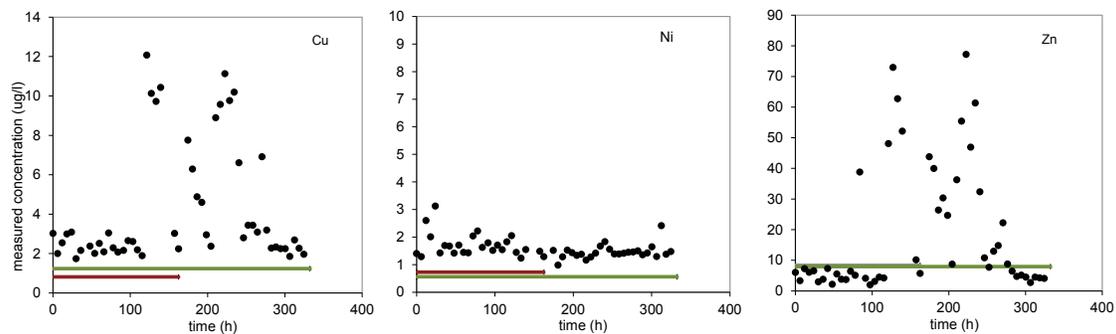


Figure 26. Dissolved metal concentrations (Cu, Ni and Zn from left to right) from automatic grab sampling (●) and TWA concentrations derived from the passive sampler (solid horizontal lines) (from Paper V).

7.1.3 Screening of wide range pollutants

In addition to the previously mentioned criteria, Chemcatcher® passive sampler was shown to be a reliable monitoring technique for a wide range of pollutants – metal species and inorganic anions. The possibility to screening for pollutants further makes the technique appropriate for a holistic monitoring that is also one of the future goals of the water directives.

7.2 Specific monitoring tasks

Passive samplers like the Chemcatcher® and DGT have a clear defined role in monitoring tasks in the context of policy frameworks such as the WFD.

It was therefore the intent of the present work to show the suitability of the passive samplers as alternative or in combination to the traditional grab sampling for attaining a better water quality monitoring. The higher quality information provided by the integrative and selective approach of passive samplers will provide information with higher precision and confidence to decision makers. As concluding remarks of the present work a list was created which summarizes the monitoring activities where passive samplers may readily be used with advantage over grab sampling (see Table 4).

Table 4. Identification of monitoring tasks suitable for the use of passive samplers in the context of a policy framework, such as the WFD.

Monitoring objective / activity	Type of monitoring
measurement of time-integrated concentrations	Surveillance, operational and investigative
assessment of long-term trends in levels of pollutants, and differences between water bodies	Surveillance
screening for presence or absence of pollutants (sometimes with improved LOD)	Surveillance, operational and investigative
speciation of contaminants	Surveillance, operational and investigative
identification of sources of pollution	Investigative

integrated assessment of pollutant load across national Surveillance
boundaries

8 Challenges for a wide acceptance and usage in monitoring programs

Passive sampling in aqueous media is potentially a cheap, useful tool that provides information on total pollution load that would be difficult and/or expensive to obtain by other means.

8.1 Specificity

Specificity is inherent to the design of all passive accumulation samplers, which means that the results produced with such devices will be specific for that device only, and highly dependent on the speciation of the analyte. While specificity is often desirable, it might also be a drawback, as results from an individual passive sampler device can be difficult to interpret, and may appear inconsistent, when compared to conventional methods. This problem may be magnified by the many different devices and configurations, often sampling different fractions, which are described in the literature.

Here, one challenge may be to communicate an easily understandable, straightforward definition of what species a particular passive sampler accumulates, preferable directly related to an established method, such as grab sampling / filtration.

8.2 Legislation

A challenge for policymakers and scientists will be how to incorporate passive accumulation sampler methods into the legislation framework and to set guideline values (EQC) that are based on solid scientific evidence and fit in with the holistic approach of the WFD.

8.3 Standardization

Steps have been taken to assess and ensure the applicability and quality of data produced by passive samplers, including the publication of the British Standards Institute's (BSI) standard method *Determination of priority pollutants in surface water using passive sampling* (BSI PAS 61:2006) and *Water quality -- Sampling -- Part 23: Guidance on passive sampling in surface waters* (ISO 5667-23 : 2011) [100]. Further efforts are needed, however, if passive samplers are to become a standard inventory in the toolbox for regulatory monitoring.

It is the opinion of the author that this technique is well developed and understood, and that most of the remaining obstacles to a more widespread adoption in the monitoring community lay in communicating the knowledge produced by the scientific community to the intended audience of policymakers, managers and operational staff, who administrate and execute regulatory monitoring programs.

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