REPORT SNO 5989-2010

RiverPOP 2009:

Measuring concentrations of persistent organic pollutants and trace metals in Norwegian rivers

Norwegian Institute for Water Research
– an institute in the Environmental Research Alliance of Norway

REPORT

Main Office
Gaustadalléen 21
NO-0349 Oslo, Norway
Phone (47) 22 18 51 00
Telefax (47) 22 18 52 00
Internet: www.niva.no

Regional Office, Sørlandet
Televeien 3
NO-4879 Grimstad, Norway
Phone (47) 22 18 51 00
Telefax (47) 37 04 45 13

Regional Office, Østlandet
Sandvikaveien 41
NO-2312 Ottestad, Norway
Phone (47) 22 18 51 00
Telefax (47) 62 57 66 53

Regional Office, Vestlandet
Thormøhlens gate 53 D
NO-5006 Bergen Norway
Phone (47) 22 18 51 00
Telefax (47) 55 31 22 14

Regional Office Central
Pirsenteret, Havnegata 9
P.O.Box 1266
NO-7462 Trondheim
Phone (47) 22 18 51 00
Telefax (47) 73 54 63 87

Title	Report No..	Date
RiverPOP 2009: Measuring concentrations of persistent organic pollutants and trace metals in Norwegian rivers RiverPOP 2009: Konsentrasjoner av persistente organiske forurensninger og metaller i norske elver	5989-2010	20.02.2010
	Project No. O-29257	Pages Price 39
Author(s) Ian J. Allan, Øyvind A. Garmo, Christopher Harman, Alfhild Kringstad and Erling Bratsberg	Topic group Marine contaminants	Distribution Fri
	Geographical area Oslo	Printed NIVA

Client(s)	Client ref.
Klima- og forurensningsdirektoratet (Klif)	TA-2662/2010

Abstract

A performance evaluation of a range of techniques for the measurement of the concentration of persistent organic pollutants and trace metals was undertaken in the Rivers Glomma and Drammen in 2009. This work focussed on further evaluating techniques that have the potential to substantially improve the reliability and limits of detection of such measurements. Passive sampling techniques were employed to measure dissolved concentrations of polycyclic aromatic hydrocarbons, polychlorinated biphenyls and brominated flame retardants while continuous flow centrifugation and time-integrative suspended particulate matter samplers were used to measure contaminants associated with the particulate phase. Contaminant limits of detection were in the low pg L^{-1} range or below and significant improvements in the sampling procedures and in the reliability of the data were observed. These methods have the potential to become a vital part of the RID monitoring programme for the evaluation of riverine fluxes of contaminants to the North Sea.

4 keywords, Norwegian	4 keywords, English
1. RID program	1. RID programme
2. Konsentrasjon av organiske miljøgifter	2. POPs and metal concentrations
3. Passive prøvetakene	3. Passive sampling
4. Sedimentfeller	4. Suspended particulate matter

Ian J. Allan
Project manager

Kristoffer Næs
Research manager

Bjørn Faafeng
Senior Adviser

ISBN 978-82-577-5724-3

O-29257

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Preface

This report presents results of a study commanded by Klif that aimed to further test and apply novel methodologies for the measurement of trace levels of persistent organic pollutants and metals in surface waters. Laboratory and fieldwork in the Drammen (Mjøndalen Bru) and Glomma (Sarpsborg) Rivers was undertaken by NIVA researchers in 2009. The data from this study supports the data from the first RiverPOP project (TA-2521/2009) and confirms that some of these technologies may have their place in the toolbox of those in charge of studies such as the Riverine Inputs and Direct Discharges monitoring programme (RID) aiming to estimate riverine fluxes of contaminants.

Members of NIVA staff who contributed to the success of this work included Christopher Harman, Øyvind A. Garmo, Alfhild Kringstad and Erling Bratsberg. Many thanks go to Erik Bjerknes and Ingar Becsan for the help with the organisation of the fieldwork and particularly with the production of the suspended sediment samplers.

We are grateful to Jon Fuglestad from the Klima- og forurensningsdirektoratet (Klif) who accompanied us and contributed to the fieldwork and to staff at Hafslund AS at Sarpsborg for letting us use their facilities for our measurements. We are also very grateful to Christine Daae Olseng from Klif for the guidance with the RiverPOP work.

Oslo, 20th February 2010

Ian J. Allan

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Summary

The measurement of riverine fluxes of trace contaminants into the North Sea is one of the overall aims of the Riverine Inputs and Direct Discharges (RID) monitoring programme. Main challenges of this work include the ability to detect and quantify trace organic contaminants and metals at very low concentrations and to obtain reliable measures of their average concentrations in water. A number of tools aiming to measure concentrations of contaminants either in the dissolved phase or associated with suspended particulate matter were tested during a fieldwork campaign in the Drammen River in 2008. The present study aimed to further evaluate some of these tools and techniques in the River Glomma in 2009.

Considering the complexity of riverine environments and the concentration levels of many of the contaminants of interest, the techniques selected for this study (and that conducted in 2008) involved more temporally representative sampling and amelioration of the limits of detection particularly when compared with commonly used bottle sampling. Most sampling methodologies tested during this study focussed on the measurement of contaminants associated with either suspended particulate matter (SPM) or those freely dissolved in water. Passive sampling was used for the measurement of trace levels of nonpolar organic contaminants such as polycyclic aromatic hydrocarbons (PAHs), polychlorinated biphenyls (PCBs) and polybrominated diphenylether (PBDEs) in the dissolved phase. Other methodologies such as the use of continuous-flow centrifugation or time-integrative suspended particulate matter samplers aimed at the measurement of these contaminants associated with SPM. Passive sampling was also applied to the measurement of the labile fraction of metals in water and data from the samplers were compared with total and filtered concentrations measured by bottle sampling. The levels of both contaminants and SPM were very low in the Drammen River and this rendered the use and comparison of data particularly challenging. It was decided that promising techniques would be further evaluated in 2009 in the Glomma River where levels of contaminants and SPM may be higher.

A range of passive sampling devices to measure freely dissolved contaminant concentrations were tested through 2 to 6 week long exposures using different designs for the passive sampler deployment units. The use of an alternative cage design here together with the specific characteristics of the sampling site in Sarpsborg achieved higher sampling rates than those observed during deployment in the Drammen River. This, in turn, allowed significantly improved limits of detection for PAHs, PCBs and PBDEs. These were in the low pg L^{-1} range or below. An improvement in the reliability of the passive sampling measurement of PBDE was also obtained.

Four replicates of a new design of time-integrative suspended particulate matter sampler (based on a sedimentation process) were produced during this project and deployed for four weeks in the River Glomma. This deployment was successful and enabled the collection of significant amounts of suspended particulate matter for the measurement of a wide range of compounds. In addition, suspended particulate matter-water partition coefficients for a number of contaminants could be estimated for the River Glomma. Concentrations of suspended particulate matter-associated contaminants measured with these samplers were in agreement with those measured by continuous-flow centrifugation. Both types of sampling procedures appear to provide similar information.

Trace metals were measured by passive sampling in the River Glomma using two versions of the Diffusion Gradient in Thin film device (DGT) and data was compared with filtered concentrations measured by spot sampling and those predicted by speciation modelling with WHAM (Windermere Humic-Aqueous Model), a model designed to calculate equilibrium chemical speciation in surface and ground waters, sediments and soils. The model is particularly suitable for problems where the chemical speciation is dominated by organic matter (humic substances). WHAM combines Humic

Ion-Binding Model V with a simple inorganic speciation code for aqueous solutions. Precipitation of aluminium and iron oxides, cation-exchange on an idealised clay mineral, and adsorption-desorption reactions of fulvic acid are also taken into account. The importance of ion accumulation in the diffuse layers surrounding the humic molecules is emphasised. Successive DGT deployments demonstrated that temporal variations in labile metal concentrations were low and that DGT-measured concentrations were 2-10 times lower than those measured by filtration. Comparisons with speciation modelling helped explaining the DGT data in most cases.

A 28 day exposure of three types of passive samplers was undertaken in the Drammen River to initiate a long-term dataset for PAH monitoring in this river at the RID monitoring programme site. Fieldwork was undertaken at a similar time of the year as in 2008 and similar passive sampling rates were obtained. PAH concentrations were of a similar level as those measured in 2008.

The reliability of the data obtained here was significantly improved when compared with the study conducted in the Drammen River. Overall, these data combined with those obtained in the Drammen River in 2008 and the relatively large body of evidence available in the scientific literature further highlight that these tools can be used for the reliable measurement of contaminant concentrations in water with a view to estimate their riverine fluxes.

Passive sampling methods using LDPE membranes, silicone strips or SPMDs are particularly well suited to the measurement of trace organic contaminants dissolved in water. These passive sampling devices can be recommended for use in monitoring programme such as RID. Further sampler selection, however, is strongly dependent on the characteristics of the analytes of interest (e.g. moderately hydrophobic vs. highly hydrophobic contaminant for example, or for analytes for which control of blank data is challenging, e.g. PBDEs). The consistency of data obtained for SPM-associated contaminants measured by continuous-flow centrifugation or using the time-integrative suspended particulate matter samplers combined with extremely performant LODs indicate that these methods may also be used in the RID monitoring programme. An important aspect of the selection of methods for monitoring of contaminants within the RID programme is the logistics (and its cost) of the implementation of these potential tools. The implementation of time-integrative suspended particulate matter samplers or of large volume water samplers may pose additional difficulties due to the scale of the RID programme and the specific characteristics of the tools and of their deployment procedures. Other methods such as passive sampling are relatively more straightforward; however, training of non-specialist fieldworker may be required.

1. Introduction

The measurement of total contaminant fluxes in riverine systems is a useful task to help estimating the overall input of contaminant into water bodies of interest and undertake mass balances. Such tasks are included in a number of regulatory monitoring programmes. For example the measurement of contaminant fluxes across national boundary is of particular importance for countries sharing river basins and large river systems such as the Danube or Rhine rivers. The assessment of the overall riverine input of contaminants into coastal waters and seas of the OSPAR region is the primary aim of the Riverine Inputs and Direct Discharges programme (RID).

In 2008, The Norwegian Pollution Control Authority (SFT) commanded a study in the Drammen River to evaluate a number of techniques aiming to improve the reliability of estimates of trace contaminant fluxes from Norwegian rivers into the North Sea [1]. Considering the complexity of riverine environments and levels of many of the contaminants of interest, the techniques selected for this study involved more temporally representative sampling and amelioration of the limits of detection particularly when compared with commonly used passive sampling [2]. Most sampling methodologies tested during this study focussed on the measurement of contaminants associated with either suspended particulate matter (SPM) or those freely dissolved in water. Passive sampling was used for the measurement of trace levels of nonpolar organic contaminants such as polycyclic aromatic hydrocarbons (PAHs), polychlorinated biphenyls (PCBs) and polybrominated diphenylether (PBDEs) in the dissolved phase [1-4]. Other methodologies such as the use of continuous-flow centrifugation or time-integrative suspended particulate matter samplers aimed at the measurement of these contaminants associated with SPM. Passive sampling was also applied to the measurement of the labile fraction of metals in water and data from the samplers were compared with total and filtered concentrations measured by bottle sampling [1, 4-6]. The levels of both contaminants and SPM were very low in the Drammen River and this rendered the use and comparison of data particularly challenging. It was decided that promising techniques would be further evaluated in 2009 in the Glomma River where levels of contaminants and SPM may be higher.

The aim of this study was to further evaluate previously identified promising techniques for the measurement of trace contaminant concentrations in water with a view to estimate their fluxes. To this end, the River Glomma and the RID monitoring site in Sarpsborg were selected for this study. Objectives were to:

- Expose passive sampling devices (low density polyethylene membranes, silicone strips and semipermeable membrane devices) using an alternative cage design in order to maximise sampling rates for PAHs, PCBs and PBDEs.
- Measure SPM-associated contaminants using the continuous-flow centrifuge and maximise the amount of particulate matter collected by increasing the sampling time.
- Develop, improve and expose time-integrative SPM samplers for the measurement of SPM-associated contaminants and based on the original version designed during the previous study.
- Measure repeatedly the labile concentration of a range of trace metals with passive sampling using two versions of the Diffusive Gradient in Thin film device (DGT) and compare the data obtained with data from regular bottle sampling and metal speciation modelling undertaken with WHAM.
- Initiate a long term passive sampling dataset by exposing LDPE membranes, silicone strips and SPMDs in the Drammen River to measure the freely dissolved concentration of PAHs.

2. Methods and procedures

2.1 Fieldwork and site description

The site chosen for this particular study is the RID programme monitoring site on the River Glomma in Sarpsborg (see figure below). Coordinates for this site are 59°16'34"N and 11°7'53"E.
The passive sampling and suspended particulate matter sampling were conducted on the Hafslund AS hydropower generation site since it provided secured areas for the deployment of the continuous-flow centrifuge, the passive sampling devices and the time-integrative SPM samplers. Our specific interests in this site were the relatively high water velocity encountered (> 2 m s^{-1}) and constant and unidirectional water flow for exposure of the SPM samplers and passive sampling devices.
A second site nearby was used for the collection of spot samples for the measurement of trace metals and the deployment of DGT passive sampling devices (see map below).

Figure 1. *Sampling site on the River Glomma in Sarpsborg (photo from wikiMapia; www.wikimapia.org).*

2.2 Sampling techniques for the measurement of nonpolar organic contaminants in the dissolved phase

Many types of passive sampling devices exist and the first RiverPOP project conducted in 2008 aimed to evaluate the possibility of using LDPE membrane and silicone strip samplers as relatively more simple alternatives to SPMDs [1, 3, 7-9]. This work also aimed to assess the comparability of the data obtained. In order to continue this work, these three different types of passive sampling devices were therefore used in this study in the Glomma River in 2009.
Batches of LDPE membranes and silicone strips were prepared in the laboratory following procedures described previously [1]. These samplers were spiked with series of deuterated and fluoroPAHs to be used as performance reference compounds (PRCs). In order to further reduce the variability in PRC concentrations (already < 10 %) between samplers, samplers of each type were all exposed to the same

methanol/water solution spiked with PRCs, rather than each sampler exposed to a its own spiking solution.
In order to maximise sampling rates, flat cages made of stainless steel mesh were used for the deployement of the samplers (see figures below). These are expected to allow significantly higher turbulences around the samplers when compared with more commonly employed "SPMD cages" and spider holders. Such turbulences are expected to promote significant increases in sampling rates and consequently lower limits of detection for analytes of interest.
Six samplers of each type (including SPMDs) were deployed in the river on the 30th September 2009 using the flat stainless steel cages. A first batch of samplers was retrieved on the 15th October after a two-week long exposure. All SPMD samplers were damaged and contained water as a result of the reasonably harsh environment they were exposed to. One sampler was also lost and remaining silicone strip and LDPE membrane samplers from the 2 week exposure period were retrieved. Replicate silicone and LDPE samplers remained in the water and were exposed until the 12th November 2009. Additional replicate silicone and LDPE samplers were deployed in standard SPMD cages on the 15th October and were exposed alongside the other cages until retrieval on the 12th November 2009.

***Figure 2**. Passive sampler deployment setup using flat stainless steel cages to maximise turbulences around the samplers (left) and cages two weeks later with very little or inexistent biofouling. All samplers suffered significantly.*

All successfully retrieved passive sampling devices including trip control samplers were extracted and analysed in the laboratory at NIVA for PRCs (deuterated PAHs and fluoroPAH), PAHs, PCBs and PBDEs following procedures previously described [1].

2.3 Sampling techniques for the measurement of nonpolar organic contaminants associated with suspended particulate matter

Time-integrative SPM samplers were initially produced for the RiverPOP project [1], however their relatively large size and heavy weight resulted in challenging conditions for their deployment and retrieval from the water. A smaller sized version of these samplers was produced preserving the same length/diameter ratio of the main cylinder as the original version (see figures below). However the length was reduced to 1 m. The diameter of the inlets and outlets was increased to 8 mm to minimise possibilities of clogging with particulate matter and algal growth.
These samplers were deployed on the 30th September and were retrieved on the 12th November 2009. Upon retrieval, in/outlets were plugged to prevent losing the water present inside the samplers and

samplers brought back to NIVA. The continuous-flow centrifuge was used to process the water from inside the samplers.

Figure 3. *Frame for the deployment of the time-integrative SPM sampler (left) and 4 SPM samplers ready for deployment (right).*

Figure 4. *Deployed time-integrative SPM samplers.*

The continuous-flow centrifuge was also used to collect SPM from the Glomma River. The Hafslund AS site was also used for this sampling since it provided a secure site. Procedures previously described [1] were also used here. The use of secure site made it possible to significantly increase the sampling time to allow the collection of relatively high masses of SPM. It was possible to run the centrifuge for up to 5 days continuously. Two samples were collected on the 15th and 28th October 2009. Another improvement when compared with the original RiverPOP project was the collection of the SPM sample from the centrifuge bowl. Since large samples were collected, it was possible to directly freeze dry, the centrifuge bowl and collect the freeze dried SPM sample ready for extraction and analysis.

2.4 Sampling techniques for the measurement of trace metals in water

Sampling for trace metals included here the use of two versions of the DGT sampler, one with the standard open pore (OP) gel and another less common version with a restricted pore (RP) gel. It is assumed that the RP version generally samples smaller metal complexes than the OP version. Sampling was also undertaken to measure filtered metal concentrations. Filtration was undertaken on site. Exposures of DGT were restricted to two weeks and were undertaken for three consecutive periods. All techniques have previously been described [1].

2.5 Additional work in the Drammen River

Few long-term monitoring datasets using passive sampling devices exist. Since work was conducted in 2008, additional passive sampling could be conducted in 2009 to complement data obtain in 2008. The advantage of the present work is the development of a long-term dataset using not one but three types of samplers alongside. Therefore replicate LDPE membranes, silicone strips and SPMDs were exposed at the RID monitoring site on the Drammen River from the 14th October to the 11th November 2009. Standard SPMD cages and spider holders were used to replicate the study conducted the year before.

2.6 Work log and timetable

The work log and timetable is provided below.

Aug. 2009	Preparation of passive samplers (14 silicone strips and 14 LDPE membranes) Preparation of four time-integrative suspended particulate matter samplers
29 Sept.	Deployment of the first set of DGTs, Collection of water samples (+filtration) for main ions and for metal concentrations Deployment of the continuous-flow centrifuge
30 Sept.	Retrieval of the centrifuge (failed sampling due to grass clogged the tubing) Deployment of 4 time-integrative SPM samplers Deployment of 6 SPMDs, 6 Silicones and 6 LDPE in flat stainless steel cages
14 Oct.	Replicate LDPE membranes, silicone strips and SPMD deployed in the Drammen River
15 Oct.	Retrieval of DGT sampler, Deployment of new DGT samplers Collection of water samples for filtered concentration of trace metals, and for main ions (+ TOC/DOC) Set-up of the continuous-flow centrifuge Retrieval of LDPE membrane and silicone strip samplers Failed SPMDs Deployment of replicate LDPE membrane and silicone strip samplers using “SPMD cages”
19 Oct.	Retrieval of the continuous-flow centrifuge Improve the fixing of the SPM samplers in the water
27 Oct.	Centrifuge bowl was freeze dried and SPM collected. Collection of approximately 6 g of SPM dry weight
28 Oct.	Set up of the continuous-flow centrifuge for sampling of the Glomma River
28 Oct.	Retrieval of DGT samplers Collection of water samples for the measurement of trace metal concentrations and for main ions (+ TOC/DOC) Deployment of DGT samplers
11 Nov.	Retrieval of LDPE membranes, silicone strips and SPMD for the Drammen River
12 Nov.	Retrieval of LDPE membranes and silicone strips (deployed in the flat cages) Retrieval of LDPE membranes and silicone strips from SPMD cage Retrieval of 4 time-integrative SPM samplers Retrieval of the final set of DGT samplers Collection of water samples for trace metal concentrations and for main ions (+ TOC/DOC)

3. Results and discussion

3.1 Passive sampling for the measurement of PAHs, PCBs and PBDEs in the River Glomma

3.1.1 Dissipation of performance reference compounds and sampling rates

PRC dissipation could be observed for both types of samplers and for LDPE membrane almost complete offload could be seen for PRC with log K_{ow} ~ 5.2. Under 40 % of fluoro-chrysene was seen to remain in LDPE membranes after the 6 week exposure in flat cages. For both types of samplers, PRC concentrations remaining after the 2 week exposure in flat cages or 4 week exposure in "SPMD cages" were similar and this indicates that sampling rates were generally higher for exposure in flat cages. This can be seen in the tables below. The within sampler-type variability of the PRC concentrations in the samplers following exposure were in the range 0.4-21.2 and 1.2-7.4 % for silicone strips and LDPE membranes, respectively.

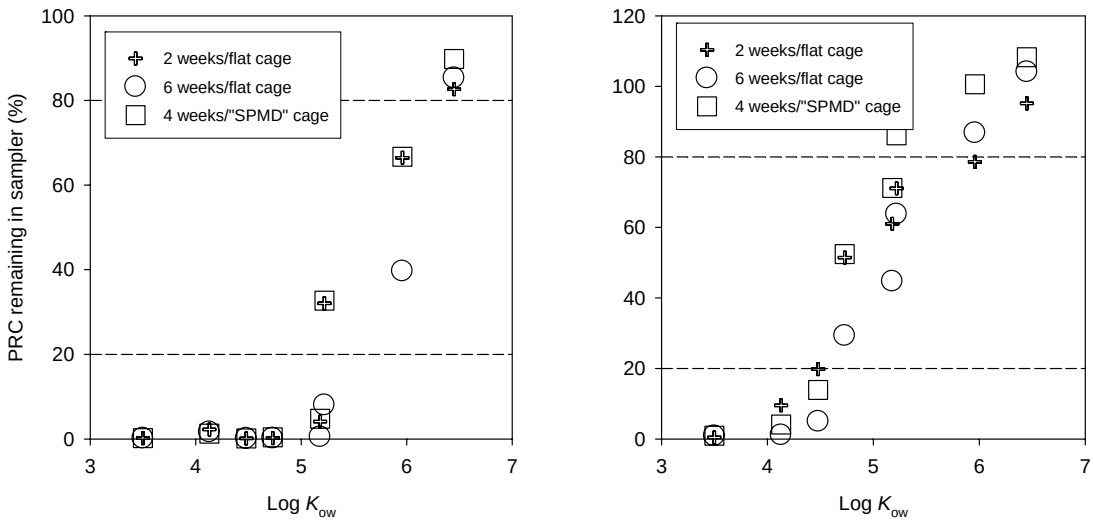

***Figure 5**. PRC remaining in samplers (%) for LDPE membrane samplers (left) and silicone strips (right) exposed for 2, 4 and 6 weeks using flat cages and conventional "SPMD cages".*

Sampling rates for LDPE membrane and silicone strip samplers were derived from PRC dissipation rates using the following equation:

$$R_s = K_{sw}\, m\, k_e$$

with the sampler-water PRC partition coefficient (L kg^{-1}) K_{sw}, m the mass of the sampler (g) and k_e the first-order PRC dissipation rate (d^{-1}). K_{sw} values for LDPE and silicone materials were taken from the literature [10] for deuterated PAHs. Those for F-PAHs are not known and estimates were calculated from those for non-deuterated PAHs. The uncertainty of this procedure is unknown.

***Table 1**. Sampling rates R_s (L d^{-1}) for LDPE membrane samplers exposed in the River Glomma*

	Log K_{sw}	Sampling rates R_s (L d^{-1})		
		2 week exposure Flat cage	6 week exposure Flat cage	4 week exposure "SPMD cage"
Fluoranthene-d_{10}	4.85	**32.7** (*1.0*)	**18.2** (*0.4*)	**15.6** (*0.2*)
F-Pyrene	5.14	22.7 (*0.5*)	16.9 (*0.2*)	11.2 (*0.3*)
F-Chrysene	5.88	44.7 (*1.0*)	33.9 (*0.6*)	22.2 (*1.8*)
Note: Since log K_{sw} values have not been measured for F-PAHs, sampling rates from these PRC are subject to significant uncertainty (K_{sw} values given here are calculated based on those for PAHs and are only rough estimates) Note: In bold are the sampling rates used for the calculation of C_w				

***Table 2**. Sampling rates R_s (L d^{-1}) for silicone strip samplers exposed in the River Glomma*

	Log K_{sw}	Sampling rates R_s (L d^{-1})		
		2 week exposure Flat cage	6 week exposure Flat cage	4 week exposure "SPMD cage"
Fluoranthene-d_{10}	4.56	**19.0** (*7.5*)	**10.1** (*0.1*)	**6.5** (*1.9*)
F-Phenanthrene	4.25	12.5 (*3.3*)	7.6 (*0.2*)	6.1 (*0.4*)
F-Pyrene	4.72	19.1 (*11.7*)	8.1 (*0.8*)	4.1 (*1.3*)
Note: Since log K_{sw} values are have not been measured for F-PAHs, sampling rates from these PRC are subject to significant uncertainty (K_{sw} values given here are calculated based on those for PAHs and are only rough estimates) Note: In bold are the sampling rates used for the calculation of C_w				

Sampling rates generally appear higher for LDPE membranes than silicone strips. However, significant uncertainty remains as a result of K_{sw} values used to calculate R_s. Masses of PAHs, PCBs and PBDEs accumulated in the various devices will provide more insight and are presented in the following section.

3.1.2 Contaminant masses absorbed in LDPE membranes and silicone strips

Trip controls and control samplers are important particularly when working with analytes such as PBDEs that are present in very low concentrations in water. The alteration of procedures for the preparation of the samplers in the laboratory led to significantly lower blank contamination with PAHs and PBDEs compared with previous work [1]. This is crucial for analytes such as PBDEs for which accumulation is low due to relatively low sampling rates and low dissolved analyte concentrations in water. Only naphthalene was found in LDPE samplers while for unknown reasons B*k*F was found in all trip control silicone strip samplers. Trip controls for PCBs and PBDEs for silicone strips and LDPE membranes were excellent with only one silicone strip trip control where CB28, BDE99 and BDE100 were found at concentrations near limits of detection.

Masses of all analyte classes accumulated in LDPE membrane samplers showed very low variability (mostly <<10 %). Silicone strips showed a considerably lower variability in masses of analytes accumulated than that associated with PRC data.

Masses of PAHs absorbed in LDPE membranes and silicone strips were in the range 6-245 ng $sampler^{-1}$. Those for silicone strips were 7-630 ng $sampler^{-1}$. Masses absorbed by the two types of samplers for the most hydrophobic compounds are similar while for the least hydrophobic compounds, larger amounts are found in silicone samplers. As shown by the PRC release, analytes with log K_{ow} < 5.2 are close to equilibrium for most exposures of LDPE membranes while sampling may remain linear for silicone strips. If equilibrium is reached for silicone, their larger volume enables higher masses to be absorbed compared with LDPE membranes.

In addition, silicone strips demonstrate that these samplers may be able to provide reliable data (or as reliable as the K_{sw} value is) for naphthalene since masses absorbed (at equilibrium) are much higher than those in the blanks.

Table 3. *PAH masses absorbed into LDPE membrane samplers during exposure of 2, 4 and 6 weeks in flat cages and standard "SPMD cages". Standard deviation (sd) is in brackets*

		Mass absorbed (ng LDPE membrane^{-1}) (*sd*)		
	Trip Control	2 week exposure Flat cage	6 week exposure Flat cage	4 week exposure SPMD cage
NAP	7.6	8.1 (*0.8*)	6.7 (*0.1*)	7.0 (*0.4*)
ACY	<5		5.9 (*0*)	5.5 (*0.4*)
ACE	<5			
FLUE	<5		7.3 (*0.1*)	8.5 (*0.5*)
DBTHIO	<5			
PHE	<5	36 (*2*)	66 (*1.4*)	76 (*1*)
ANT	<5		9.1 (*0.5*)	9.1 (*0.3*)
FLUO	<5	100 (*0*)	240 (*0*)	260 (*0*)
PYR	<5	79 (*2*)	245 (*7.1*)	235 (*8*)
B*a*A	<5	13.3 (*1*)	69 (*0*)	54 (*3*)
CHRY	<5	29 (*1*)	130 (*0*)	99 (*2*)
B*bj*F	<5	21 (*5*)	93.5 (*0.7*)	61 (*6*)
B*k*F	<5 (*43*)	47 (*11*)	71.0 (*4.2*)	55 (*6*)
B*e*P	<5	10.7 (*2*)	43 (*1.4*)	26 (*3*)
B*a*P	<5	10.1 (*2*)	29 (*0.7*)	19 (*3*)
PeR	<5	10.6 (*1.6*)	29 (*1.4*)	13.5 (*0.7*)
In*123cd*P	<5		7.0 (*0.1*)	
DB*ah*A	<5			
B*ghi*P	<5		6.4 (*0*)	

Table 4. *PAH masses absorbed into silicone strip samplers during exposure of 2, 4 and 6 weeks in flat cages and standard "SPMD cages". Standard deviation (sd) is in brackets*

		Mass absorbed (ng silicone strip^{-1}) (*sd*)		
	Trip Control	2 week exposure Flat cage	6 week exposure Flat cage	4 week exposure SPMD cage
NAP	15	55 (*11*)	120 (*14*)	140 (*0*)
ACY	<5	18 (*4*)	51 (*3*)	57 (*2*)
ACE	<5	34 (*6*)	43 (*1*)	48 (*3*)
FLUE	<5	61 (*11*)	140 (*0*)	149 (*2*)
DBTHIO	<5	10.5 (*2.3*)	21 (*0*)	19 (*0*)
PHE	<5	250 (*50*)	630 (*14*)	605 (*8*)
ANT	<5	14.3 (*3.5*)	53 (*2*)	46 (*1*)
FLUO	<5	150 (*30*)	565 (*8*)	430 (*0*)
PYR	<5	83 (*18*)	370 (*0*)	285 (*8*)
B*a*A	<5	7.3 (*1.2*)	51 (*1*)	41 (*1*)
CHRY	<5	15 (*3*)	89 (*10*)	68 (*7*)
B*bj*F	<5	12 (*3*)	72 (*6*)	46 (*9*)
B*k*F	15	25 (*8*)	35 (*2*)	28 (*3*)
B*e*P	<5	6.9 (-)	30 (*2*)	17 (*2*)
B*a*P	<5		14 (*0*)	7.3 (*0.4*)
PeR	<5	7.9 (*1.3*)	22 (*0*)	11 (*0*)
In*123cd*P	<5			
DB*ah*A	<5			
B*ghi*P	<5			

PCB concentrations appear to be very low in the River Glomma. Only a few ng of CB118 and CB153 were found in LDPE membranes and silicone strips following the 6 week exposure under high turbulences. Pentachlorobenzene, hexachorobenzene and *p,p'*-DDE were found in LDPE membranes while silicone strips also enabled significant accumulation of γ-HCH, OCS, *p,p'*-DDD and α-HCH. Masses absorbed in the samplers are likely to be close to equilibrium for LDPE sampler while the large volume of the silicone strips allowed absorption of larger amounts of these analytes and their concentrations to be above limits of detection.

Table 5. *PCB and organochlorine masses absorbed into LDPE membrane samplers during exposure of 2, 4 and 6 weeks in flat cages and standard "SPMD cages". Standard deviation (sd) is in brackets*

		Mass absorbed (ng LDPE membrane^{-1}) (*sd*)		
	Trip Control	2 week exposure Flat cage	6 week exposure Flat cage	4 week exposure SPMD cage
CB28	<1			
CB52	<1			
CB101	*I*			
CB118	<1		1.1 (*0.1*)	
CB105	<1			
CB153	<1		1.2 (*0.1*)	
CB138	<1		1.1	
CB156	<1			
CB180	<1			
CB209	<1			
PeCB	<0.5	0.6	0.6 (*0*)	0.7 (*0*)
α-HCH	<1			
HCB	<0.5	4.8 (*0.1*)	8.0 (*0*)	7.1 (*0.3*)
γ-HCH	<1			
OCS	<1			
p,p'-DDE	<1	1.5 (*0.1*)	3.2 (*0.1*)	1.9 (*0.1*)
p,p'-DDD	<2			

Table 6*. PCB and organochlorine masses absorbed into silicone strip samplers during exposure of 2, 4 and 6 weeks in flat cages and standard "SPMD cages". Standard deviation (sd) is in brackets*

		Mass absorbed (ng silicone strip^{-1}) (*sd*)		
	Trip Control	2 week exposure Flat cage	6 week exposure Flat cage	4 week exposure SPMD cage
CB28	23	23 (*3*)	25 (*9*)	12 (*4*)
CB52	<1		1.3 (*0*)	
CB101	*I*			
CB118	<1		2.4 (*0.1*)	1.5 (*0.1*)
CB105	<1			
CB153	<1		1.0	
CB138	<1			
CB156	<1			
CB180	<1			
CB209	<1			
PeCB	<0.5	1.6 (*0.4*)	4.2 (*0.1*)	2.7 (*0.1*)
α-HCH	<1	4.2 (*0.7*)	4.5 (*0.3*)	5.4 (*0.1*)
HCB	<0.5	30 (*10*)	56 (*15*)	38 (*11*)
γ-HCH	<1	7.8 (*1.6*)	9.3 (*0.4*)	11 (*1*)
OCS	<1	38 (*11*)	175 (*7*)	160 (*14*)
p,p'-DDE	<1	1.1	3.3 (*0.2*)	1.8 (*0.1*)
p,p'-DDD	<2		3.2 (*0.1*)	

BDE47, BDE99 and BDE100 were reliably measured with LDPE membrane samplers. Trip controls were below limits of detection and the 6 week exposure resulted in masses of BDE47 absorbed that were approximately 10 x limits of detection. Only the 6 week exposure was able to result in the detection of BDE100. Data from the silicone strip samplers is mostly similar to that of LDPE membranes. One trip control sampler was shown to present concentrations of BDE99 and BDE100 in a range close to limits of detection. All other trip controls were below limits of detection. Masses of PBDEs found in silicone strip samplers are generally in the same range as those found in LDPE membranes.

Table 7. *PBDE masses absorbed into LDPE membrane samplers during exposure of 2, 4 and 6 weeks in flat cages and standard "SPMD cages". Standard deviation (sd) is in brackets*

		Mass absorbed (ng LDPE membrane^{-1}) (*sd*)		
	Trip Control	2 week exposure Flat cage	6 week exposure Flat cage	4 week exposure SPMD cage
BDE28	<0.1			
BDE47	<0.1	0.32 (*0.03*)	1.03 (*0.1*)	0.63 (*0.07*)
BDE49	<0.1			
BDE66	<0.1			
BDE71	<0.1			
BDE77	<0.1			
BDE85	<0.1			
BDE99	<0.1	0.11 (*0.02*)	0.44 (*0.02*)	0.23 (*0.02*)
BDE100	<0.1	< 0.1	0.14 (*0.1*)	< 0.1
BDE119	<0.1			
BDE138	<0.1			
BDE153	<0.1			
BDE154	<0.1			
BDE183	<0.2			
BDE205	<0.1			
BDE209	<0.5			

Table 8. *PBDE masses absorbed into silicone strip samplers during exposure of 2, 4 and 6 weeks in flat cages and standard "SPMD cages". Standard deviation (sd) is in brackets*

		Mass absorbed (ng silicone strip^{-1}) (*sd*)		
	Trip Control	2 week exposure Flat cage	6 week exposure Flat cage	4 week exposure SPMD cage
BDE28	<0.1			
BDE47	<0.1	0.21 (*0.07*)	0.74 (*0*)	0.39 (*0.02*)
BDE49	<0.1			
BDE66	<0.1			
BDE71	<0.1			
BDE77	<0.1			
BDE85	<0.1			
BDE99	<0.1 (0.1)[a]		0.20 (*0.02*)	
BDE100	<0.1 (0.13)[a]			
BDE119	<0.1			
BDE138	<0.1			
BDE153	<0.1			
BDE154	<0.1			
BDE183	<0.25			
BDE205	<0.4			
BDE209	<2			
[a] one value above limit of detection in blanks				

Sampling rates were investigated by comparing masses of analytes accumulated over different exposure times, using different types of cages and for the two types of sampling materials. As shown on the figure below, ratios of masses accumulated during the 6 week exposure over those absorbed during the two week exposure (6 week/2 week) were consistent for both materials and varied between 1 and 2 depending on analyte hydrophobicity. A ratio of 1 could be expected when analyte uptake has reached equilibrium. 6 week/2 week ratios show significantly more scatter.

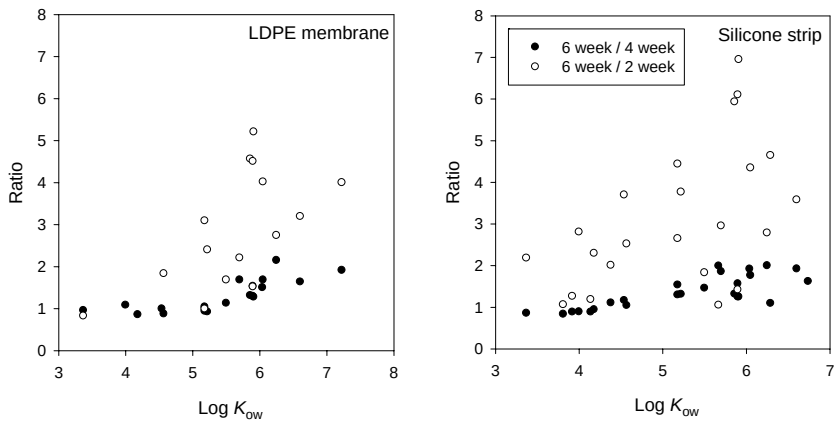

Figure 6. *Ratios of analyte masses accumulated in silicone strips and LDPE for during exposures of 2, 4 and 6 weeks wusing flat cages and the standard "SPMD cage".*

It was also possible to compare masses absorbed by the different samplers for the same exposure time (see figure below). Silicone strip/LDPE membrane ratios of masses accumulated varied between 2 and 11 for analytes with log K_{ow} < 5.5. Since sampling for many of these analytes is expected to have reached or be close to equilibrium, differences in K_{sw} values for the two sampler materials and in

volumes of the two types of sampler become significant and ratios well over 1 are expected. For analytes with log *K*ow > 5.7, ratios are generally below 1. Since samplers were of the exact same surface area and conformation and exposed in the same way, identical sampling rates and therefore masses accumulated (linear sampling far from equilibrium) for these analytes were expected. It may be that under much higher turbulences than those found during the Drammen River, it becomes more difficult to obtain identical sampler deployment and identical sampling rates. This is supported by observed differences in PRC-based estimates of sampling rates in the present study. These PRC-based estimates of sampling rates are however subject to significant uncertainty associated with K_{sw} values and the relatively high variability of masses of PRCs observed for silicone strip following exposure.

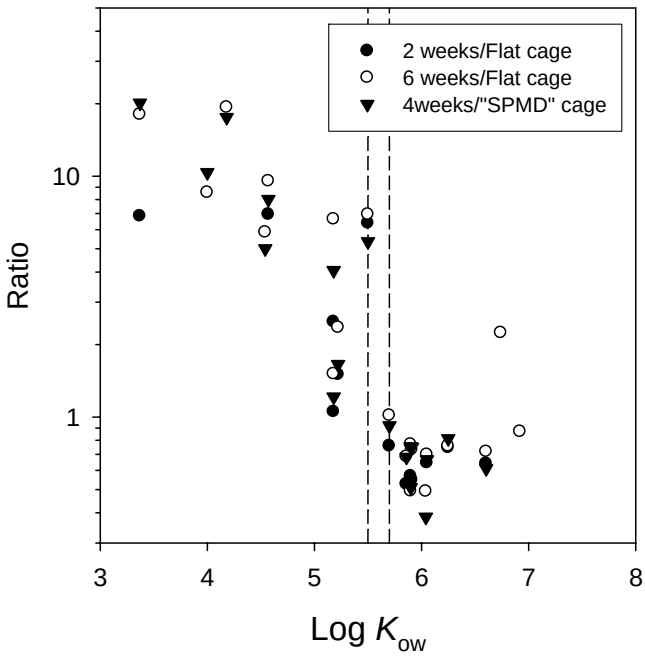

Figure 7. *Ratios of analyte masses absorbed by silicone strips to those found in LDPE membranes for sampler exposures of 2, 4 and 6 weeks using flat cages and "SPMD cages". Vertical reference lines indicate the log K_{ow} range for which transition between non linear and linear sampling occurs.*

Analyte masses were normalised to the sampling rate calculated from the dissipation of d_{10}-fluoranthene before calculating ratios of masses as above. For analyte under linear uptake, this equate to a comparison of concentrations measured by the different samplers. These new ratios are compared with original ratios in the figure below. R_s-normalised ratios close to 1 for the two week exposure indicate that differences in masses accumulated by the different sampler types could be explained by the differences in estimates of sampling rates. For the 6 and 4 week exposures, normalised ratios were found to be slightly above 1.

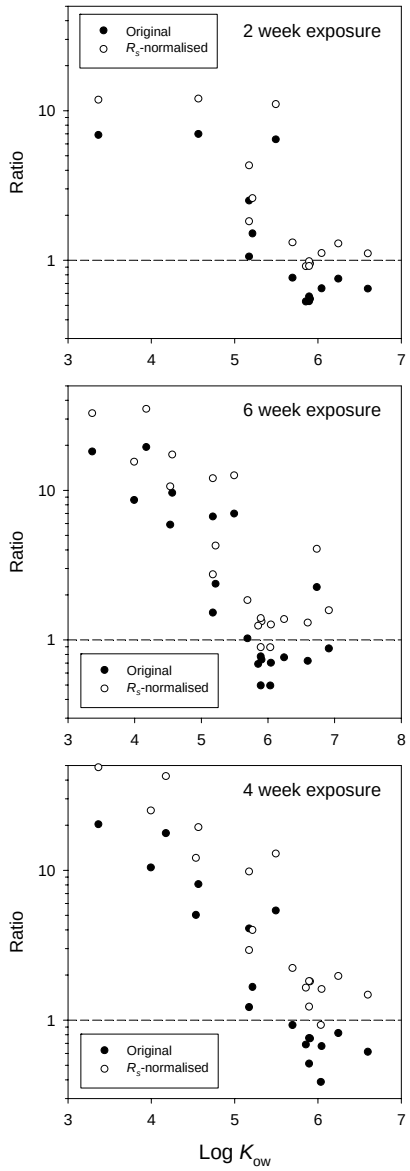

Figure 8. *Comparison of ratios of analyte masses absorbed by silicone strips to those absorbed in LDPE membranes for 2, 4 and 6 week exposures with flat cages and "SPMD cages". R_s-normalised ratios indicate that masses accumulated were normalised to PRC-based sampling rates found for each exposure and type of sampler.*

3.1.3 Dissolved concentrations of PAHs, PCBS and PBDEs in water

PRC data was used to estimate for which compounds sampling remained integrative over the exposure and those for which sampling was closer to equilibrium. The transition was found to be for analytes with log K_{ow} values between 5.2 and 5.8.

For analytes that were close to equilibrium, the concentration in water was calculated using:

$$C_w = \frac{m_{analyte} / m_{sampler}}{K_{sw}}$$

where $m_{analyte}$ is the analyte mass in the sampler after exposure (ng), $m_{sampler}$ the mass of the sampler (g) and K_{sw} the sampler-water partition coefficient (L g^{-1}).

Sampling rates deduced from d_{10}-fluoranthene PRC dissipation rates were used to calculate dissolved contaminant concentrations in water from masses absorbed into the samplers for analytes that were under linear uptake, so that:

$$C_w = \frac{m_{sampler}}{R_s\, t}$$

with R_s the sampling rate (L d^{-1}) and t the exposure time (d). Since our understanding of the generally observed decrease in sampling rates with increasing analyte hydrophobicity (when uptake is boundary layer-controlled) is limited, the application of a single sampling rate was found to be the most simple method here. While this may lead to an underestimation of dissolved concentrations, these are not likely to be significant in comparison with all other sources of uncertainty.
Dissolved concentrations of PAHs are in the low ng per litre for the least nonpolar compounds and as low as 20 pg L^{-1} for the most nonpolar compounds detected. The tables below present dissolved concentrations of all analytes detected in the various samplers for the different exposure time.

Based analytical limits of detection, the 6-week exposure of LDPE membranes and silicone strips resulted in "field" limits of detection of 0.7 and 2 pg L^{-1} for PCBs, respectively. Values for PBDEs were in the range 0.1-0.2 pg L^{-1} while those for BDE209 were higher and in the range 2-3 pg L^{-1}. These are generally well below limits of detections obtained for the deployment in the Drammen River in 2008.

Table 9. *PAH concentrations in water measured by LDPE membrane samplers during exposure of 2, 4 and 6 weeks in flat cages and standard "SPMD cages". Standard deviation (sd) is in brackets*

	C_w (ng L^{-1}) (*sd*)		
	2 week exposure Flat cage	6 week exposure Flat cage	4 week exposure SPMD cage
NAP	6.2	5.1	5.4
ACY		2.0	1.9
FLUE		0.62	0.72
PHE	1.1	2.0	2.3
ANT		0.21	0.21
FLUO	0.6	1.4	1.5
PYR	0.31	0.97	0.93
B*a*A	0.029	0.050	0.059
CHRY	0.062	0.095	0.11
B*bj*F	0.045	0.068	0.067
B*k*F	0.10	0.052	0.060
B*e*P	0.023	0.031	0.028
B*a*P	0.022	0.021	0.021
PeR	0.023	0.021	0.015

Table 10. *PAH concentrations in water measured by silicone strip samplers during exposure of 2, 4 and 6 weeks in flat cages and standard "SPMD cages". Standard deviation (sd) is in brackets*

	C_w (ng L^{-1}) (*sd*)		
	2 week exposure Flat cage	6 week exposure Flat cage	4 week exposure SPMD cage
NAP	3.5	7.7	9.0
ACY	0.68	1.9	2.1
ACE	0.56	0.70	0.79
FLUE	0.7	1.6	1.7
DBTHIO	0.07	0.13	0.12
PHE	1.3	3.4	3.2
ANT	0.06	0.22	0.19
FLUO	0.56	1.3	2.4
PYR	0.3	0.9	1.6
B*a*A	0.027	0.12	0.22
CHRY	0.056	0.21	0.37
B*bj*F	0.044	0.17	0.25
B*k*F	0.093	0.083	0.15
B*e*P	0.026	0.071	0.093
B*a*P		0.033	0.040
PeR	0.030	0.052	0.060

Low concentrations of dissolved PCBs were measured since, despite the relatively high sampling rates, only the 6 week long exposure of LDPE membranes allowed the detection of some PCBs at concentrations below 1 pg L^{-1}. Concentration estimates given by silicone strip samplers were higher than estimates provided by LDPE membranes. A difference of a similar order of magnitude was observed for estimates of dissolved concentrations of hexachlorobenzene by LDPE membranes and silicone strips. However, better agreement between estimates for *p,p'*-DDE is found.

Table 11. *PCB and organochlorine concentrations in water measured by LDPE membrane samplers during exposure of 2, 4 and 6 weeks in flat cages and standard "SPMD cages". Standard deviation (sd) is in brackets*

	C_w (pg L^{-1}) (*sd*)		
	2 week exposure Flat cage	6 week exposure Flat cage	4 week exposure SPMD cage
CB118		0.77	
CB153		0.84	
CB138		0.80	
HCB	10.4	5.8	7.8
p,p'-DDE	3.2	2.3	2.1
Note: PeCB concentration could not be calculated due to the unavailability of K_{sw} value			

Table 12. *PCB and organochlorine concentrations in water measured by silicone strip samplers during exposure of 2, 4 and 6 weeks in flat cages and standard "SPMD cages". Standard deviation (sd) is in brackets*

	C_w (pg L^{-1}) (*sd*)		
	2 week exposure Flat cage	6 week exposure Flat cage	4 week exposure SPMD cage
CB52		3.1	
CB118		5.5	8.0
CB153		2.4	
PeCB	5.9	9.8	14.8
α-HCH*	*70*	*74*	*89*
HCB	114	131	209
γ-HCH*	*85*	*101*	*114*
OCS**	*142*	*413*	*880*
p,p'-DDE	4.1	7.7	9.6
p,p'-DDD		7.5	

*Analytes for which equilibrium was attained but for which K_{sw} values are not available. Values for PAH with similar log Kow were used instead (Note: this results in relatively uncertain C_w)
**Values for octachlorostyrene appear very high and are not in agreement with the LDPE data

Generally, few PBDEs were detected in the samplers. Dissolved concentrations of BDE47, BDE99 and BDE100 measured with LDPE membranes were below 1 pg L^{-1}. Those measured by silicone strips are slightly higher but remain in good agreement.

Table 13. *PBDE concentrations in water measured by LDPE membrane samplers during exposure of 2, 4 and 6 weeks in flat cages and standard "SPMD cages". Standard deviation (sd) is in brackets*

	C_w (pg L^{-1}) (*sd*)		
	2 week exposure Flat cage	6 week exposure Flat cage	4 week exposure SPMD cage
BDE47	0.70	0.75	0.69
BDE99	0.24	0.32	0.25
BDE100		0.10	

Table 14. *PBDE concentrations in water measured by silicone strip samplers during exposure of 2, 4 and 6 weeks in flat cages and standard "SPMD cages". Standard deviation (sd) is in brackets*

	C_w (ng L^{-1}) (*sd*)		
	2 week exposure Flat cage	6 week exposure Flat cage	4 week exposure SPMD cage
BDE47	0.78	1.7	2.1
BDE99		0.47	

In order to compare the concentration estimates provided by the two types of samplers, mean concentrations were calculated for each contaminant from concentrations from both samplers and all exposure times. The deviation (%) of concentrations measured by the two types of samplers from the mean was calculated for each analyte and this data was used to prepare the box-plot presented below.

This shows that LDPE membranes tend to underestimate mean concentrations, while silicone strips appear to overestimate mean concentrations. Overall concentrations measured by the two types of samplers are within a factor of 2 of mean values.

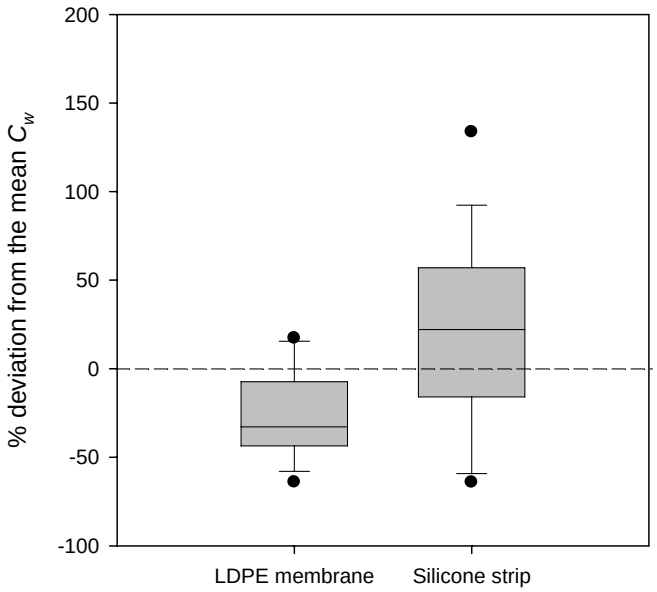

Figure 9. *Box-plot of the % deviations of contaminant concentrations measured by the two types of samplers from the mean of concentrations from all samplers and exposure times.*

Dissolved concentrations of PAHs in the River Glomma at Sarpsborg do not appear to be significantly different from those measured in the Drammen River. However, many more PAHs are detected using these samplers as a result of the higher sampling rates for exposures in the Glomma River [1]. A few PCBs and organochlorines were detected in the River Glomma as a result of the high sampling rates and the relatively long 6-weeks exposure. All concentrations were below limits of detection for the 28 day exposure of SPMDs in the River Drammen in 2008. The same PBDEs were generally detected in both rivers (i.e. BDE47, BDE99 and BDE100) and concentrations were of the same order of magnitude. However the reliability of the data from the study in the River Glomma is much higher since BDE levels in trip control samplers were below limits of detection and samplers were able to accumulate BDE amounts approximately 4 to 10 times higher than the limits of detection.

3.2 Concentrations of PAHs, PCBs and PBDEs on the suspended particulate matter in the River Glomma

3.2.1 Measurements of concentrations

Relatively larger amounts of suspended particulate matter were collected from the River Glomma both using the centrifuge and the time-integrative SPM sampler compared with those collected in the River Drammen in 2008 [1]. The ability to deploy the centrifuge for periods of 2 to 5 days significantly helped to increase the recovery of SPM. Levels of SPM in the water were measured twice and were found to be 6.3 and 1.6 mg L^{-1}. While these appeared relatively variable, they are generally higher than those measured in the Drammen River. This allowed more reliable chemical analysis due to the adequate size of the SPM samples. Samples were extracted and analysed for a suite of PAHs, PCBs and PBDEs. Most PAHs were above limits of detection and concentrations measured in the different samples generally varied by less than a factor of three. The TOC level for the three SPM samples varied between 3 and 5 %. The variability associated with differences in measured concentrations can be the result of the analyis, the different sampling times and changes in SPM concentrations over time. Therefore, the variability of concentrations measured here for SPM-associated contaminants is totally

acceptable. Most PCBs were below limits of detection with limits of detection generally between 0.3 and 1 ng g^{-1} dry weight of SPM. CB153, pentachlorobenzene (PeCB), hexachlorobenzene (HCB) and *p,p'*-DDE were detected in some but not all samples.
Estimate of whole water concentrations of PAHs associated with SPM were generally < 200 pg L^{-1} in the River Glomma. Limits of detection for SPM-associated PCBs were in the close to 2 pg L^{-1}.

Table 15. *Concentrations of PAHs (ng g^{-1}) associated with suspended particulate matter sampled through continuous-flow centrifugation and using the time-integrative suspended particulate matter sampler*

	Contaminant concentrations in suspended particulate matter samples (ng g^{-1})		
	Centrifugation		Time-integrative sampler
	S-1	S-2	S-1
Date	19/10/09	28/10/09	12/11/09
TOC (µg C mg^{-1})	50.1	42.5	**31.2**
NAP	10	9.1	6.1
ACY	<2	2.6	<2
ACE	<2	<2	<2
FLUE	3.5	4.6	2.8
DBTHI	<2	2.7	<2
PHE	22	33	19
ANT	3.2	2.5	2.8
FLUO	29	43	28
PYR	22	35	24
B*a*A	10	21	9.6
CHRY	16	32	12
B*bj*F	27	65	19
B*k*F	9.7	23	7.1
B*e*P	16	35	13
B*a*P	12	26	11
PER	43	43	22
*In123cd*P	13	37	8.5
DB*ah*A	2.5	6.2	<2
B*ghi*P	13	34	8.8

Table 16. *Concentrations of PCBs and organochlorines (ng g^{-1}) associated with suspended particulate matter sampled through continuous-flow centrifugation and using the time-integrative suspended particulate matter sampler*

	Contaminant concentrations in suspended particulate matter samples (ng g^{-1})		
	Centrifugation		Time-integrative sampler
	S-1	S-2	S-1
Date	19/10/09	28/10/09	12/11/09
TOC (µg C mg^{-1})	50.1	42.5	**31.2**
CB28	<0.5	<0.5	<0.5
CB52	<0.5	*i*	<0.5
CB101	*i*	*i*	*i*
CB118	<0.5	<0.5	<0.5
CB105	<0.5	<0.5	<0.5
CB153	<0.5	**0.62**	<0.5
CB138	<0.5	<0.5	<0.5
CB156	<0.5	<0.5	<0.5
CB180	<0.5	<0.5	<0.5
CB209	<0.5	<0.5	<0.5
PentaCB	**0.72**	**1.6**	<0.3
α-HCH	<0.5	<0.5	<0.5
HCB	**0.32**	**0.44**	<0.3
γ-HCH	<0.5	<0.5	<0.5
OCS	<0.5	<0.5	<0.5
p,p'-DDE	<0.5	**0.72**	<0.5
p,p'-DDD	<1	<1	<1

Table 17. *Concentrations of PBDE (ng g^{-1}) associated with suspended particulate matter sampled through continuous-flow centrifugation and using the time-integrative suspended particulate matter sampler*

	Contaminant concentrations in suspended particulate matter samples (ng g^{-1})		
	Centrifugation		Time-integrative sampler
	S-1	S-2	S-1
Date	19/10/09	28/10/09	12/11/09
TOC (µg C mg^{-1})	50.1	42.5	31.2
BDE28	**0.05**	<0.1	**0.1**
BDE47	**0.20**	**0.56**	<0.1
BDE49	<0.05	0.16	<0.05
BDE66	<0.1	<0.2	<0.1
BDE71	<0.05	<0.1	<0.05
BDE77	<0.05	<0.1	<0.05
BDE85	<0.05	<0.1	<0.05
BDE99	<0.1	<0.4	<0.1
BDE100	<0.05	<0.15	<0.05
BDE119	<0.05	<0.1	<0.05
BDE138	<0.05	<0.1	<0.05
BDE153	<0.05	<0.1	<0.05
BDE154	<0.05	<0.1	<0.05
BDE183	<0.1	<0.2	<0.1
BDE196	<0.1	<0.2	<0.1
BDE205	<0.05	<0.1	<0.05
BDE209	<12	<4	<1

3.2.2 Contaminant partitioning in the River Glomma

A number of compounds were detected and quantified both in the dissolved phase and associated to suspended particulate matter. This allowed the calculation of suspended particulate matter-water partition coefficients for PAHs, some PCBs, organochlorines and BDEs in the overlying water phase. These coefficients were normalised to the fraction of organic carbon, f_{oc} in the suspended particulate matter (on average 4 % at the Glomma River) to obtain K_{poc} for PAHs for example:

$$K_{poc} = \frac{C_{SPM-PAH}}{C_{w-PAH} \cdot f_{oc}}$$

where K_{poc} is the particulate organic carbon-normalised SPM-water partition coefficient for a PAH compound, $C_{SPM-PAH}$ and C_{w-PAH} the PAH concentrations associated with SPM and those dissolved in water, respectively. For PAHs, log K_{poc} values are generally well correlated with log K_{ow} values. The slope of the linear log K_{poc}-log K_{ow} regression was 0.97 (standard error = 0.08, R^2 = 0.958) with an intercept of 1.11. A few log K_{poc} values were calculated for PCBs and other organochlorines. For most analytes except HCB, log K_{poc} values are slightly higher than log K_{ow} values.

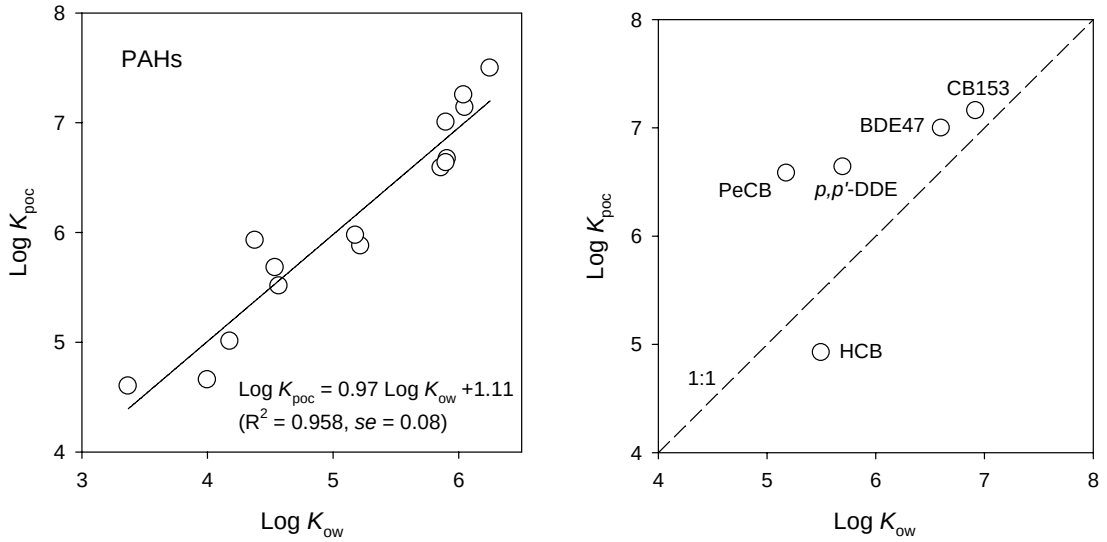

Figure 10. *Estimates of particulate organic carbon-normalised suspended particulate matter-water partition coefficients (log K_{poc}) for PAHs (left) and PCBs, HCB, PeCB, p,p'-DDE and BDE47 (right) in the River Glomma.*

3.3 Measurements of trace metal concentrations with DGT and modelling of metal speciation with WHAM

The DGT labile concentrations (C_{DGT}) presented are calculated using:

$$C_{DGT} = \frac{M\left(\frac{\Delta \mathrm{gel}}{\mathrm{D_{gel}}} + \frac{\Delta \mathrm{f}}{\mathrm{D_f}} + \frac{\delta}{\mathrm{D_w}}\right)}{\mathrm{A}t}$$

where M is the mass of metal accumulated during the deployment time, Δgel, Δf and δ are the thicknesses of the hydrogel, filter and diffusive boundary layer, respectively, D_{gel}, D_f and D_w are the corresponding diffusion coefficients, A sampler effective area and t is the deployment time [11, 12].

The DGT measured concentrations of inorganic metal presented in the figure below are obtained following the procedure described below. It is assumed that there is no kinetic restriction and that diffusion coefficients of inorganic metal and metal bound by humic substances can be represented by single values. This is of course a simplification of reality where diffusion coefficients and dissociation rate constants are distributed over a range of values (see e.g. [13]).

1. The concentration of inorganic metal is assumed to be equal to C_{DGT} measured using restricted-pore hydrogels (i.e., metal complexes with humic substances are assumed to be unavailable for uptake) [14, 15].
2. The contribution of metal bound by humics to the mass accumulated in open-pore DGTs is derived as the difference between total mass accumulated in open-pore DGTs minus the mass attributable to inorganic species (using C_{DGT} from step 1 and rearranging equation x).
3. The concentration of metal bound by humic substances is calculated using equation x, ignoring the diffusive boundary layer, and the mass obtained in step 2. Diffusion coefficients of humic substances were obtained from [12] and corrected for temperature using the expression given in [16]. Fulvic acid and humic acid were assumed to constitute 90% and 10%, respectively, of the humic substances.

Calculation of the chemical speciation of metals in the river was performed using WHAM [17], incorporating Humic Ion-Binding Model VI [18]. Calculations were based on main parameters and concentrations measured in filtered samples, except for Al where input was defined by the solubility product of aluminium hydroxide. The concentration of humic substances was derived from DOC measurements: 50% of the measured DOC was assumed to be humic substances, which were themselves assumed to be 50% carbon (Suwannee river fulvic acid is 52% C). Fulvic acid and humic acid were assumed to constitute 90% and 10%, respectively, of the humic substances.

The figure below shows the results obtained for Al, Mn, Ni, Cu, Zn, and Cd at the sampling site in River Glomma. The panels show concentrations in filtered water samples obtained at 4 different dates. Horizontal lines show concentrations of DGT labile metal species integrated over 3 deployment times (September 29th – October 15th, October 15th – October 28th, and October 28th – November 12th). The different colours represent sampling with standard DGTs containing an open pore hydrogels (green) and DGTs containing a hydrogel with smaller pores (red), restricting the diffusion of high molecular weight species. The measured concentrations of trace metals are close to background levels and do not indicate significant temporal variation except, perhaps, for a slight increase in Mn and Zn towards the end of the monitoring. Results obtained with DGT are 2-10 times lower than concentrations measured in filtered water samples, reflecting that a significant fraction of metal was present in the form of colloids or slowly dissociating complexes able to pass through the 0.45 µm filter, but unavailable for DGT.

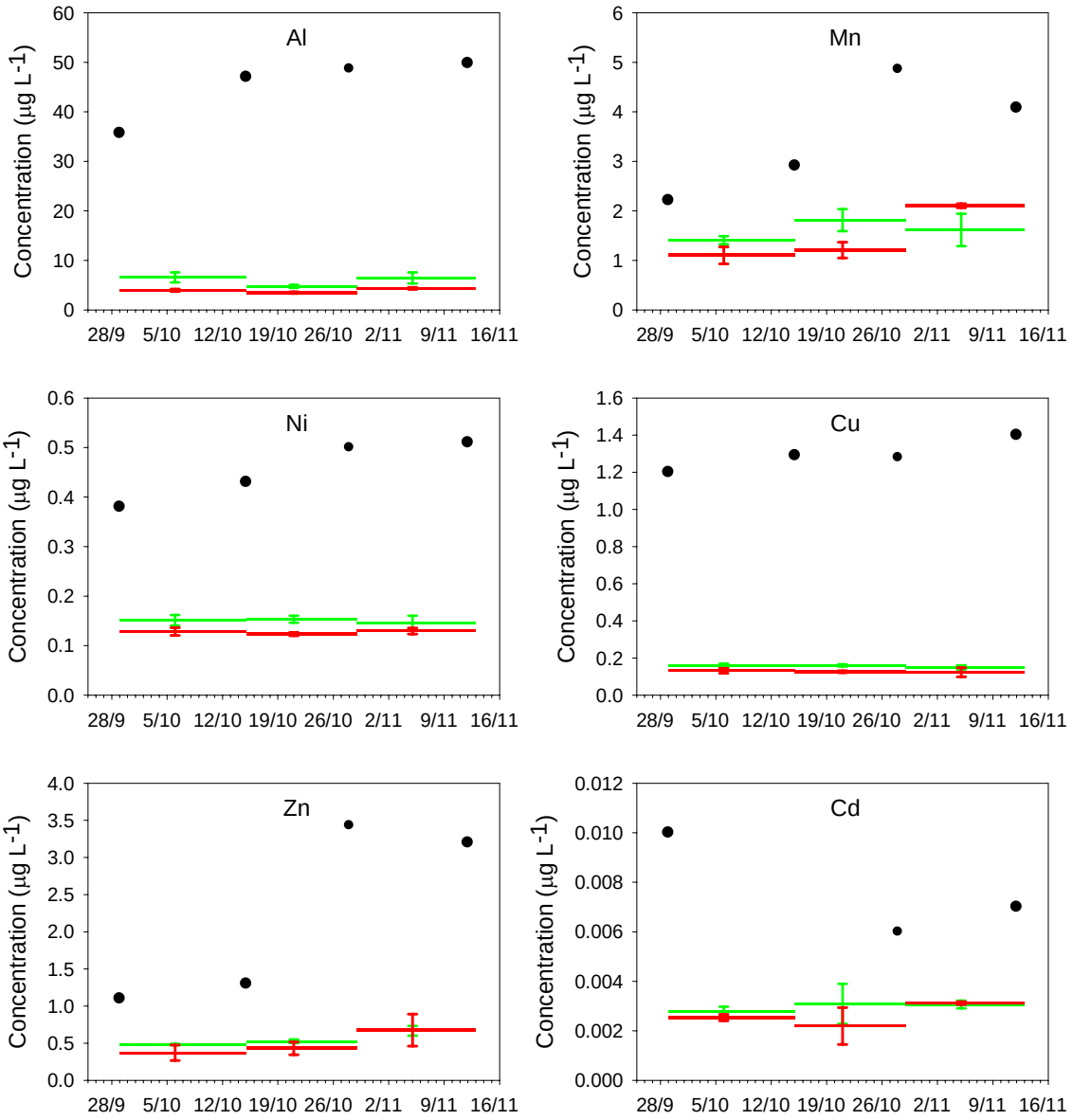

Figure 11. *Concentrations in filtered water samples (dots). Horizontal lines show concentrations of DGT labile metal species integrated over 3 deployment times. The different colours represent sampling with standard DGTs containing an open pore hydrogels (green) and DGTs containing a hydrogel with smaller pores (red).*

The total concentrations of DGT labile metal, which are larger than the DGT-labile concentrations presented in the figure below, and the proportion of metal present as low molecular weight species (i.e. free metal and small inorganic complexes) and high molecular weight species (i.e. colloids assumed to be complexes with humic substances) can be estimated from the difference between the results obtained with open-pore and restricted-pore DGTs provided that the diffusion coefficients of low and high molecular weight metal species can be represented by single mean values and that all metal species are assumed to be fully labile. In the figure below metal concentrations and distribution between small inorganic species and humic substances based on DGT results are compared with metal distribution predicted by WHAM speciation modelling. It is clear that accounting for the lower diffusion coefficients of metal complexed by humic substances greatly reduces the differences

between the DGT labile and filterable fraction for all metals except Cu. There is also a relatively good agreement between ratios of metal bound by humic substances as estimated from DGT measurements and those predicted by WHAM. The exception is again Cu which WHAM predicts to be almost fully complexed by humics. The reason for the deviating results for Cu is not clear. It could be that WHAM overestimates the humic fraction of Cu. It could also be that the assumptions on which the DGT derived fractions are based, are erroneous.

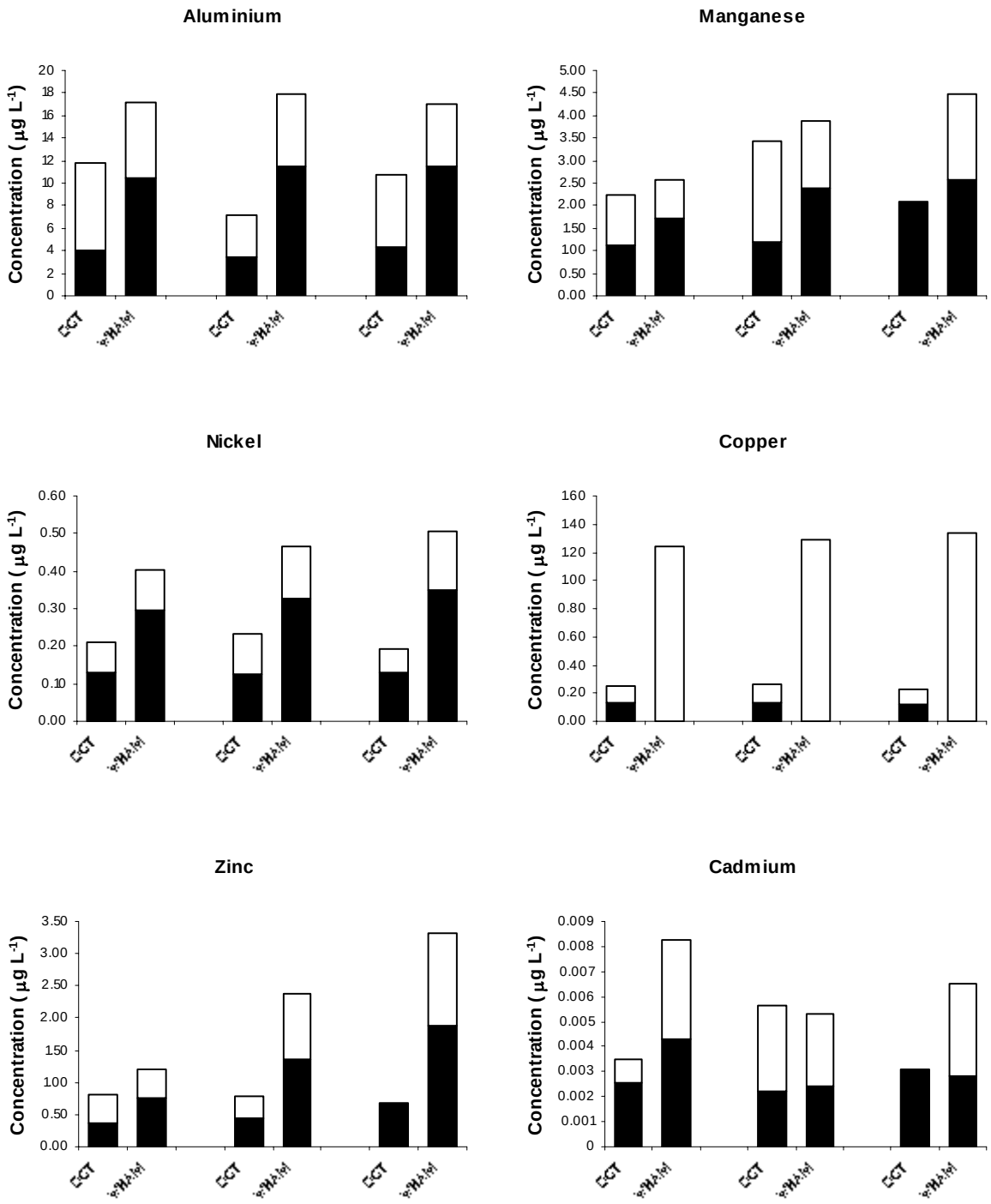

Figure 12. Concentration of inorganic species of metal (black) and metal bound by humic substances (white) estimated from DGT and WHAM

3.4 Passive sampling measurement in the Drammen River

Samplers were deployed in the River Drammen for 28 days for the measurement of dissolved concentrations of PAHs in the overlying water. The month-long deployment of LDPE membranes and silicone strips led to the significant dissipation of a number of performance reference compounds as shown in the figure below where % dissipation are shown as a function of the log K_{ow} of PRCs (the source of approximate log K_{ow} values for fluoroPAHs (F-PAH) was www.chemspider.com). While PRC dissipation was shown to be almost complete for some PRCs, for others dissipation was within the recommended 20-80 % dissipation.

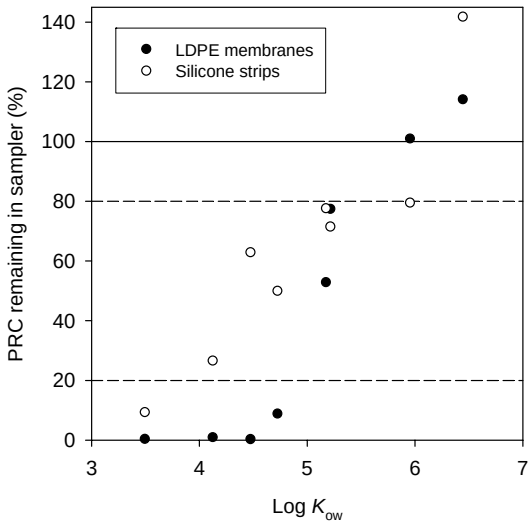

Figure 13. *% Dissipation of performance reference compounds (d_{10}-fluorene, d_{10}-fluoranthene and fluoroPAHs) spiked in LDPE membranes and silicone strips during a 28 day exposure in the Drammen River.*

Sampling rates, R_s, were derived from PRC dissipation rates using the following equation:

$$R_s = K_{sw}\, m\, k_e$$

with the sampler-water PRC partition coefficient (L kg^{-1}) K_{sw}, m the mass of the sampler (g) and k_e the first-order PRC dissipation rate (d^{-1}). K_{sw} values for LDPE and silicone materials were taken from the literature [10]. Results are given in the table below and generally show that sampling rates for all three samplers are of a similar order of magnitude. For analytes with log K_{ow} in the range 4-5.2, R_s values vary in the range 2.5-6.8 L d^{-1}. Sampling rates observed here are similar to those obtained under similar conditions of deployment (site, mooring, cage, water temperature) in the Drammen river in 2008 [1]. These were in the range 1.9 to 6.1 L d^{-1} and depended on the PRC compound.

Table 18. *Sampling rate estimates from the dissipation of PRCs (deuterated PAHs and fluoroPAHs) for LDPE membranes, silicone strips and SPMDs exposed for 28 days in the Drammen River*

		Sampling rate (R_s, L d^{-1})		
PRC compound	Log K_{ow}	LDPE Membrane	Silicone strip	SPMD
Fluorene-d_{10}	4.13	*1.34*[b,c]	4.22	
Fluoranthene-d_{10}	5.18	3.27	*5.48*	
F-Naphthalene	3.50[a]	*0.37*	1.81	-
F-Biphenyl	4.48[a]	*6.57*	3.41	-
F-Phenanthrene	4.73[a]	4.13	6.74	-
F-Pyrene	5.22[a]	2.56	*9.98*	-
F-Chrysene	5.96[a]	-	-	-
F-Benzo(*k*)fluoranthene	6.45[a]	-	-	-

[a] Values estimated with software on www.chemspider.com
[b] Sampling rates based on PRC dissipation outside the 20-90 % range are given in *italic*
[c] F-PAH sampling rates calculated based on K_{sw} values extrapolated from K_{ow} and K_{sw} for non-fluorinated analogues

The median value of PRC-based sampling rates was used to calculate dissolved PAH concentrations for the Drammen River. Median values were 3.27 and 3.87 L d^{-1} for LDPE membranes and silicone strips, respectively. These are much lower than those observed during the deployment in the River Glomma. Concentrations are generally in agreement with those obtained in 2008 [1].

Table 19. *Dissolved concentrations of PAHs in the Drammen River measured during 28 day exposures of LDPE membranes and silicone samplers*

	PAH concentration (ng L^{-1}) (*sd*)	
	LDPE membrane	Silicone strip
NAP	6.3 (*0.7*)	6.9 (*0*)
ACY	<1.7	1.3
ACE	<0.6	0.19 (*0*)
FLUE	0.56 (*0.03*)	0.35 (*0.01*)
DBTHIO	<0.23	<0.06
PHE	2.0 (*0.09*)	0.86 (*0.03*)
ANT	0.14	0.07 (*0*)
FLUO	1.4 (*0.03*)	0.69 (*0.22*)
PYR	1.2 (*0.03*)	1.09 (*0.4*)
B*a*A	0.25 (*0.04*)	0.08 (*0.04*)
CHRY	0.36 (*0.06*)	0.13 (*0.06*)
B*bj*F	0.32 (*0.06*)	0.19 (*0.03*)
B*k*F	0.41 (*0.07*)	0.32 (*0.10*)
B*e*P	0.13 (*0.01*)	0.07
B*a*P	0.24 (*0.01*)	<0.05
PeR	<0.055	<0.05
In*123cd*P	<0.055	<0.05
DB*ah*A	<0.055	<0.05
B*ghi*P	<0.055	<0.05

3.5 Comparison of contaminant concentrations measured during this study with those measured through the RID monitoring programme

Sampling in the Glomma was also undertaken in 2009 as part of the RID monitoring programme. Sampling was conducted on a monthly basis and Table 20 provides a summary of contaminant concentrations measured from September to November 2009, period during which the present study was conducted. Whole water concentrations (total concentrations) of trace metals and organic contaminants are measured during the RID programme while those measured with many of the methods tested in the present study are based on the measurement of contaminants in either the dissolved phase (passive samplers), filtered (filtration of water samples for the measurement of trace metals) and those associated with suspended particulate matter (continuous flow centrifugation and time-integrative suspended sediment samplers).
DGT-labile concentrations of Cd, Cu, Ni, Pb and Zn are generally much lower than filtered concentrations measured in the present study (Figure 11) but also when compared with those measured during the RID programme (Table 20). However, total concentrations of these trace metals measured through the RID monitoring programme appear very consistent with filtered concentrations measured here (Figure 11).

Concentrations of PCBs and lindane (γ-HCH) in "whole water" samples collected with the RID monitoring programme were all below limits of detection, 0.2 ng L^{-1}. The use of silicone strips and LDPE membranes for the passive sampling of PCBs in the dissolved phase resulted in the detection and quantification of a number of PCBs. Concentrations of CB52, CB118, CB153, CB138 were in the range 0.8-8 pg L^{-1} in the dissolved phase. Limits of detection for PCBs were below 1 pg L^{-1} and this is 200 times lower than those that can be achieved with bottle sampling. The concentration of lindane measured based on data from silicone strips samplers was in the range 0.08-0.12 ng L^{-1} and this is close to or slightly below the limit of detection of the bottle sampling procedure used during the RID monitoring programme. Overall, the use of passive samplers for organic contaminants allows detection limits significantly below those that can be achieved through bottle sampling.

***Table 20**. Metallic and organic contaminant concentrations measured during the RID monitoring programme on three occasions. These sampling date correspond to those during which sampling of the RiverPOP project was undertaken.*

	Sampling date		
	07/09/2009	05/10/2009	09/11/2009
Cd (μg L^{-1})	0.007	0.008	0.01
Cu (μg L^{-1})	1.7	1.39	1.99
Ni (μg L^{-1})	0.76	0.41	0.76
Pb (μg L^{-1})	0.322	0.08	0.19
Zn (μg L^{-1})	3.46	1.9	5.91
CB28 (ng L^{-1})	< 0.2	< 0.2	< 0.2
CB52 (ng L^{-1})	< 0.2	< 0.2	< 0.2
CB118 (ng L^{-1})	< 0.2	< 0.2	< 0.2
CB153 (ng L^{-1})	< 0.2	< 0.2	< 0.2
CB138 (ng L^{-1})	< 0.2	< 0.2	< 0.2
CB180 (ng L^{-1})	< 0.2	< 0.2	< 0.2
γ-HCH (ng L^{-1})	< 0.2	< 0.2	< 0.2

4. Summary and conclusions

The measurement of riverine fluxes of trace contaminants is one of the overall aims of the RID monitoring programme. Main challenges here are the ability to detect and quantify trace organic contaminants and metals at very low concentrations and to obtain reliable measures of average concentrations. A number of tools aiming to measure concentrations of contaminants either in the dissolved phase or associated with suspended particulate matter were tested during a fieldwork campaign in the Drammen River in 2008. The present study aimed to further evaluate some of these tools and techniques in the River Glomma in 2009.

A range of passive sampling devices to measure freely dissolved contaminant concentrations were tested through 2 to 6 week long exposures using different cage designs. The use of an alternative cage design here together with the specific characteristics of the sampling site in Sarpsborg achieved higher sampling rates than those observed during deployment in the Drammen River. This, in turn, allowed significantly improved limits of detection for PAHs, PCBs and PBDEs. These were in the low pg L^{-1} range or below. An improvement in the reliability of the passive sampling measurement of PBDE was also obtained.

Four replicates of a new design of time-integrative suspended particulate matter sampler (based on a sedimentation process) were produced during this project and deployed for four weeks in the River Glomma. This deployment was successful and enabled the collection of significant amounts of suspended particulate matter for the measurement of a wide range of compounds. In addition, suspended particulate matter-water partition coefficients for a number of contaminants could be estimated for the River Glomma. Concentrations of suspended particulate matter-associated contaminants measured with these samplers were in agreement with those measured by continuous-flow centrifugation. Both types of sampling procedures appear to provide similar information.

Trace metals were measured by passive sampling in the River Glomma using two versions of the Diffusion Gradient in Thin film device (DGT) and data was compared with filtered concentrations measured by spot sampling and those predicted by speciation modelling with WHAM. Successive DGT deployments demonstrated that temporal variations in labile metal concentrations were low and that DGT-measured concentrations were 2-10 times lower than those measured by filtration.
A 28 day exposure of three types of passive samplers was undertaken in the Drammen River to initiate a long-term dataset for PAH monitoring in this river at the RID monitoring programme site. Fieldwork was undertaken at a similar time of the year as in 2008 and similar passive sampling rates were obtained. PAH concentrations were of a similar level as those measured in 2008.

Overall, these data combined with those obtained in the Drammen River in 2008 and the relatively large body of evidence available in the scientific literature further highlight that these tools can be used for the reliable measurement of contaminant concentrations in water with a view to estimate their riverine fluxes. Passive sampling methods using LDPE membranes, silicone strips or SPMDs are particularly well suited to the measurement of trace organic contaminants dissolved in water. These passive sampling devices can be recommended for use in monitoring programme such as RID. Further sampler selection, however, is strongly dependent on the characteristics of the analytes of interest (e.g. moderately hydrophobic vs. highly hydrophobic contaminant for example, or for analytes for which control of blank data is challenging, e.g. PBDEs). The consistency of data obtained for SPM-associated contaminants measured by continuous-flow centrifugation or using the time-integrative suspended particulate matter samplers combined with extremely performant LODs indicate that these methods may also be used in the RID monitoring programme.
An important aspect of the selection of methods for monitoring of contaminants within the RID programme is the logistics of the implementation of these potential tools. The implementation of time-

integrative suspended particulate matter samplers or of large volume water samplers may pose additional difficulties due to the scale of the RID programme and the specific characteristics of the tools and of their deployment procedures. Other methods such as passive sampling are relatively more straightforward; however, training of non-specialist fieldworker may be required.

A few more detailed conclusions

- A very low variability in PRC spiking and contaminant masses accumulated following exposure was observed for LDPE membrane passive samplers. A slightly higher variability was found for silicone strip samplers but data remained highly acceptable.
- The higher passive sampling rates obtained in the River Glomma using the flat wide mesh stainless steel cages allowed improved sampling for most analytes. This also allowed significant improvements in limits of detection of the target compounds.
- Initial levels of contaminants in trip control samplers and blanks were mostly below limits of detection. Importantly, in most cases no PBDEs could be seen in blank/trip control samplers and masses of PBDEs absorbed during the 6 week long exposure were 4 to 10 times higher than limits of detection.
- Silicone strip passive samplers enabled the absorption of higher amounts of analytes reaching equilibrium relatively rapidly than in LDPE membranes. This was exemplified by data obtained for naphthalene and lindane for example. This is likely the result of the higher capacity of this sampler.
- FluoroPAHs appear promising for use as PRCs for passive sampling devices since dissipation of these compounds during exposure could be observed and were in agreement with the deuterated PAH data.
- The comparability of the data obtained in the River Glomma with the two types of sampler is very acceptable.
- Continuous-flow centrifugation undertaken for 2-4 days enabled the accumulation of significantly more suspended particulate matter than the 6 hour sampling in the Drammen River. This in turn has a positive impact on the reliability of the measurement of trace contaminant concentrations.
- The new design of the time-integrative suspended particulate matter sampler enabled the accumulation of relatively large amounts of SPM over a 4 week period.
- SPM-water partition coefficients were measured for PAHs, some PCBs and PBDEs. Values appeared of a correct order of magnitude.

5. References

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Appendix A. Major water quality parameters

Major water quality parameter measured on four occasions (29/09, 15/10, 28/10 and 12/11) are presented in the table below. pH and concentration of major components of water from the sampling site are presented. Alkalinity, pH, calcium nitrate and total nitrogen are relatively high compared with typical Norwegian surface waters. Temporal variations during the time span of monitoring appear to have been small.

Table 21. Major water quality parameters

Parameter	Unit	2009-09-29	2009-10-15	2009-10-28	2009-11-12
pH		7.23	6.86	7.23	7.18
Conductivity	mS/m	4.21	4.85	4.76	4.85
Alkalinity	mmol/l	0.258	0.261	0.274	0.27
Sodium	mg/l	1.32	1.44	1.21	1.64
Potassium	mg/l	0.64	0.66	0.55	0.75
Calcium	mg/l	5.4	5.5	3.99	5.49
Magnesium	mg/l	0.77	0.83	0.68	0.93
Chloride	mg/l	1.67	1.97	2.08	2.18
Sulphate	mg/l	3.53	3.73	3.46	3.82
Total organic carbon	mg C/l	3.9	3.7	4	4.1
Dissolved organic carbon	mg C/l	3.8	3.6	3.9	4.1
Total nitrogen	µg N/l	410	465	525	585
Nitrate nitrogen	µg N/l	230	280	300	345
SPM level	mg/l		6.3		1.6

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Gaustadalléen 21 • NO-0349 Oslo, Norway
Telephone: +47 22 18 51 00 • Fax: 22 18 52 00
www.niva.no • post@niva.no