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RiverPOP 2010

Measurement of trace contaminants in the Glomma River and some recommendations from RiverPOP projects (2008-2011)

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REPORT

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Abstract

An evaluation of the performance of a range of techniques for the measurement of the concentration of trace level organic contaminants was undertaken in the River Glomma during the period August-November 2010. This work focussed on further evaluating two techniques that have the potential to substantially improve the reliability and limits of detection of such measurements. Passive sampling devices, namely low density polyethylene membranes and silicone strips, were deployed over three consecutive 28 day periods to measure dissolved concentrations of polycyclic aromatic hydrocarbons, polychlorinated biphenyls and brominated flame retardants. Continuous flow centrifugation was used to measure these contaminants associated with the particulate phase. Contaminant limits of detection were in the low pg L^{-1} range or below. These methods have the potential to become a vital part of the Riverine Input and Discharge (RID) monitoring programme for the evaluation of riverine fluxes of contaminants to the North Sea and to help with responding to the challenges set by the EU Water Framework Directive (WFD). A set of recommendations for the use of these techniques for such monitoring tasks is given.

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1. RID program	1. RID programme
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Preface

This report presents results of a study commanded by the Climate and Pollution agency (Klif) and aimed to optimise sampling and protocols and analytical procedures for the measurements of concentrations of trace levels of organic contaminants in surface waters of Norwegian waters. Fieldwork was conducted in the river Glomma (Sarpsborg) by NIVA researchers in 2010.

The data obtained here supports data previously collected through RiverPOP projects (2009 and 2010) and confirms that tools tested here have a strong potential to improve the measurement of trace levels of organic contaminants in surface waters in Norway such as those conducted within the Riverine Inputs and Direct discharges monitoring programme (RID).

This report reviews the data and outcome of all the RiverPOP work (2008-2010) forming the basis for some recommendations for the use of specific tools and techniques for the measurement of contaminant levels in Norwegian rivers.

Members of staff who made this work possible include Kine Bæk, Alfhild Kringstad, Erling Bratsberg, Andreas Høgfeldt, Christopher Harman, and Øyvind Garmo.

We are grateful to Christine Daae Olseng for providing us with the means to further our understanding and possibilities regarding contaminant fate and measurements in Norwegian rivers.

Oslo, 25th February 2011

Ian J. Allan

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Summary

Summary and recommendations from the RiverPOP projects

The measurement of riverine fluxes of contaminants is an important task included in a number of monitoring programmes. The accuracy and precision of average contaminant concentrations is therefore very important for adequate estimation of these fluxes. "RiverPOP" projects were undertaken from 2008 to 2010 in the Drammen and Glomma rivers (Norway) with the aim to evaluate and optimise a number of sampling and monitoring tools and techniques that may be suitable for use within the Riverine Inputs and Discharge monitoring programme. Work was conducted to evaluate promising methodologies to improve the measurement of contaminant concentrations in water used for further estimation of contaminant fluxes in rivers, particularly when these contaminant concentrations are very low. These techniques are based on the monitoring of (operationally-defined) specific fractions of contaminants in water. These include fractions associated either with suspended particulate matter or those dissolved in water. Some techniques such as passive sampling are also able to provide time-averaged information on concentration levels. In general these techniques can provide limits of detection that cannot be achieved through conventional bottle sampling. These aspects are very pertinent to the RID monitoring programme since at present bottle sampling is the technique used for the monitoring of organic contaminants in water. Main challenges here were the ability to detect and quantify trace organic contaminants at very low concentrations and to obtain reliable measures of average concentrations.

These tools and techniques included a range of passive samplers for organic and metallic contaminants, high volume water sampling, and techniques such as continuous-flow centrifugation and time-integrative suspended particulate matter sampling with sediment traps. The reliability of the measurements of hydrophobic organic contaminant concentrations using three different types of passive samplers was assessed throughout this work. Data from the various samplers for the two rivers were found to be consistent and yielding reliable dissolved concentration estimates. Limits of detection were up to three orders of magnitude lower than those achieved through conventional bottle sampling during the RID monitoring programme. These limits of detection were maximised by increasing sampling rates (equivalent volume of water extracted per unit of time) for these samplers. Concentrations of polychlorinated biphenyls and other organochlorines (PCBs/OCs) and polybrominated diphenyl ethers (PBDEs) (when above limits of detection) were in the low pg L^{-1} or sub-pg L^{-1} range. Within-sampler type variability was low for all analytes under study and this is is an advantage for the monitoring of long-term trends and changes in concentrations. Continuous-flow centrifugation and time-integrative suspended particulate matter (SPM) samplers (sediment traps) yielded estimates of SPM-associated contaminant concentrations that were within a factor of 2-3 for PAHs. This is relatively consistent considering the differences in sampling times for these two techniques. Despite the collection of sufficient amounts of material, SPM-associated concentrations of PCBs and PBDEs were in most cases close to or below limits of detection. It was possible to measure PAHs both on the particulate and in the dissolved phase in the Glomma River, while only a few PCBs and PBDEs were found in both these phases in the two rivers. This indicates that concentrations were very low. PAH, PCB/OC and PBDE data obtained in 2009 in the River Glomma was consistent with that obtained in 2010. Deployments of Diffusive Gradient in Thin film devices (DGTs) allowed time-integrative measurements of labile metals over periods of one month and these estimates of concentrations were in agreement with speciation modelling for the two rivers.

As depicted in this report, many possibilities exist to improve the operation (field operation and sample collection and processing), limits of detection, the use of the data and its quality assurance and reliability of these tools. Overall, passive sampling data obtained during the RiverPOP projects and the

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.

We therefore recommend the use of these tools to improve estimates of time-averaged concentrations of trace hydrophobic contaminants in Norwegian rivers. These tools are particularly useful when concentrations are very low or close to background levels. The use of custom-made passive samplers may enable further improvements in limits of detection.

Ideally, passive samplers for hydrophobic compounds should be used together with a technique enabling the measurement of contaminants associated with suspended particulate matter. As long as a secure site with electrical power can be found in the vicinity of the sampling location, use of continuous-flow centrifugation is advised. It has been found to be the simplest and most performant approach to the collection of SPM samples. Considerations regarding sampling times must be based on the levels of SPM in the river and the efficiency in the centrifuge.

Diffusion Gradient in Thin film devices (DGTs) can be used for period of two to four weeks for the time-integrative measurement of labile metals in water. Ideally, measurements should be accompanied by monitoring of main water parameters that can allow speciation modelling.

While most of these measurements are of a specific fraction of contaminants in water, the estimation of fluxes will require estimates of "whole water" concentrations data. Modelling of speciation for metals or partitioning for nonpolar compounds may be used to infer these "whole water" concentrations. However, supporting data/information and water body-specific knowledge of partitioning may be required for such modelling. While such a procedure may result in some uncertainty, this has to be balanced against other uncertainties such as those arising from the measurement of water flow used in the calculation of fluxes.

Conclusions from the study performed in 2010

Based on previous work through RiverPOP projects, passive samplers and continuous-flow centrifugation aiming to measure concentrations of contaminants in the dissolved phase and associated with suspended particulate matter, respectively were tested during a field evaluation in the River Glomma in 2010. Two types of passive sampling devices were used to measure freely dissolved contaminant concentrations. Silicone strips were used for the measurement of polycyclic aromatic hydrocarbons (PAHs) and hexabromocyclododecane (HBCD) while low density polyethylene (LDPE) membranes were deployed for the measurement of PAHs, polychlorinated biphenyls and other organochlorines (PCBs/OCs) and polybrominated diphenyl ethers (PBDEs). These were exposed during three consecutive periods of 28 days in the river. A similar cage to that tested in 2009 was used here. This procedure allowed significantly improved limits of detection for PAHs, PCBs and PBDEs as a result of higher sampling rates. These were in the low pg L^{-1} range or below and consistent data was obtained for PBDEs and in particular for BDE209 during the first exposure period. The reproducibility of the measurements was within the expected range. Dissolved PAH concentrations measured by the two types of samplers were consistent. In addition, concentrations of PCBs/OCs and PBDEs measured with LDPE membranes were in agreement with those measured in 2009. Suspended particulate matter was sampled on three occasions by continuous-flow centrifugation to measure contaminant concentrations. This, in turn, allowed the estimation of suspended particulate matter-water partition coefficients for some of the contaminants of interest and these were in agreement with those measured in 2009. $\text{Log}K_{POC}$ values from 2010 are in good agreement with data obtained the year before. It was possible in 2010 to measure BDE209 both in the particulate and the dissolved phase (with LDPE membranes).

Sammendrag

Sammendrag og anbefalinger fra "RiverPOP"-prosjektene

Målinger av tilførsler av miljøgifter fra elver er viktige elementer i flere overvåkningsprogrammer. For å kunne beregne tilførsler på en mest mulig korrekt måte er det viktig at konsentrasjonen av miljøgiften måles på en presis og nøyaktig måte. RiverPOP-prosjektet som har pågått fra 2008 til 2010 i Drammenselva og Glomma, har hatt som mål å vurdere og optimalisere verktøy og teknikker som videre kan benyttes i Elvetilførselsprogrammet (RID). Metoder som ble ansett som velegnede, ble testet ut for å forbedre prøvetaking og beregning av tilførsler av spesielt miljøgifter som finnes i lave konsentrasjoner. Disse teknikkene er basert på målinger av spesifikke, operasjonelt definerte fraksjoner i vannsøylen, slike som suspendert partikulært materiale eller oppløste fraksjoner. Noen teknikker, som passive prøvetakere, kan også gi et tidsintegrert bilde av konsentrasjonsnivåene i vannsøylen. Generelt kan disse prøvetakningsmetodene gi lavere deteksjonsgrenser for konsentrasjoner av miljøgifter enn konvensjonell prøvetakning. Dette er viktige aspekter for RID-programmet, da man i dag kun benytter seg av konvensjonell prøvetakning. En av utfordringene her har vært å kunne påvise og kvantifisere miljøgifter i lave konsentrasjoner på en sikker måte.

Disse verktøyene og teknikkene inkluderer ulike passive prøvetakere for organiske og uorganiske miljøgifter, høyvolums prøvetaker, kontinuerlig vannstrømssentrifuge og sedimentfeller. Utfordringer knyttet til målinger av organiske miljøgifter i tre ulike passive prøvetakere var hovedfokus i dette arbeidet. Data fra prøvetakerne og de to elvene viste seg å være konsistente, og ga fornuftige estimerte konsentrasjoner av frie oppløste konsentrasjoner. Deteksjonsgrensene var opp til tre størrelsesordner lavere enn ved konvensjonell prøvetakning under RID-programmet. Disse deteksjonsgrensene ble maksimalisert ved å øke prøvetakningsraten (volum vann ekstrahert per tidsenhet) i prøvetakerne. Konsentrasjonene av PCB, andre klororganiske forbindelser og PBDE var i nivået pg L^{-1}. Resultatene fra de ulike prøvetakene og forskjellige miljøgiftene ga tilsvarende resultater, noe som gjør de egnede til utplasseringer i lengre tid og ved variable konsentrasjoner.

Kontinuerlig vannstrømssentifugering og tidsintegrerte prøvetakere for SPM (sedimentfeller) ga estimater av partikkelbundne miljøgifter som for PAH samsvarte innenfor en faktor 2-3. Dette er relativt konsistente resultater tatt i betraktning forskjellen i prøvetakningstiden mellom de to teknikkene. På tross av at nok materiale ble samlet inn, så var konsentrasjoner av PCB og PBDE i det suspenderte materialet i flest tilfeller nær eller like under deteksjonsgrensen. Det var mulig å måle PAH-forbindelser i både partikkelbundet og fri fraksjon i Glomma, mens bare noen få PCB- og PBDE-forbindelser ble funnet i begge de to fraksjonene i disse elvene. Data for PAH, PCB/OC og PBDE fra 2009 i Glomma samsvarte med funnene fra 2010. Utplassering av DGTer i en måned ga en tidsintegrert konsentrasjon av labile metaller i vannsøylen som tilsvarte beregninger utført med spesieringsmodeller i begge elevene.

Som beskrevet i denne rapporten er det mange muligheter til forbedring av metodene som er beskrevet, hva gjelder innsamling og bearbeiding av prøver, deteksjonsgrenser, bruk av data og kvalitetssikring av disse, samt pålideligheten til resultatene. Data fra passiv prøvetakning under RiverPOP-prosjektet og publikasjoner i internasjonale tidsskrifter viser at disse teknikkene og metodene kan benyttes for å skaffe tilveie sikre målinger av konsentrasjoner av miljøgifter i vann som kan benyttes til å beregne tilførsler av miljøgifter fra elver.

Vi anbefaler at disse verktøyene benyttes for å forbedre beregninger av tidsintegrerte konsentrasjoner av hydrofobe miljøgifter som er til stede i lave konsentrasjoner i norske elver. De er spesielt nyttige når konsentrasjonene er veldig lave og nær bakgrunnskonsentrasjoner. Bruk av spesiallagede passive prøvetakere vil kunne redusere deteksjonsgrensene ytterligere.

Ideelt sett bør passive prøvetakere for hydrofobe miljøgifter benyttes sammen med teknikker som gjør det mulig å måle miljøgifter assosiert til suspendert partikulært materiale. Så lenge det finnes tilgang til elektrisk strøm, og den kontinuerlig vannstrømssentrifuge kan plasseres på et sikkert sted ved prøvetakningspunktet, anbefales denne. Den har vist seg å være den enkleste og mest pålitelige måten å samle suspendert materiale på. Optimal prøvetakingstid må bestemmes på basis av sentrifugeeffektivitet og nivå av suspendert materiale i elva.

DGT kan utplasseres i perioder på to til fire uker for å måle et tidsintegrert bilde av den labile konsentrasjonen av metaller i vannsøyla. Ideelt bør man ta målinger av de viktigste parametrene i vann samtidig slik at man kan gjøre spesieringer ved hjelp av modeller.

Flesteparten av teknikkene som er nevnt her, måler en spesifikk fraksjon av miljøgiftene i vann. For å beregne tilførsler kreves det måling i ”alle fraksjonene”. Modellering for spesiering av metaller eller fordelingen av ikke-polare forbindelser kan brukes til å estimere ”alle fraksjonene”. Ytterligere målinger og informasjon om vannkilden, samt vannforekomst-spesifikk kunnskap om fordeling av miljøgiftene kan være nødvendig for modelleringen. Slike prosedyrer øker usikkerheten i beregningene, men dette må balanseres mot andre usikkerheter som kommer fra måling av vannføringen som brukes i tilførselsberegningene.

Konklusjoner fra arbeidet i 2010

Basert på tidligere arbeider i RiverPOP-prosjekter ble passive prøvetakere og den kontinuerlig vannstrømssentrifugen testet ut i Glomma i 2010. To typer passive prøvetakere ble benyttet til å måle den frie konsentrasjonen av miljøgifter. Silikonstrips ble benyttet for måling av PAH og HBCD, mens lav tetthets polyetylenmembraner (LDPE) ble utplassert for måling av PAH, PCB, andre klororganiske forbindelser og PBDE. Disse prøvetakerne ble plassert ut i tre påfølgende perioder av 28 dager i elva. På grunn av høyere prøvetakningsrate ble deteksjonsgrensen for PAH, PCB og PBDE forbedret. Disse var i nedre grense av pg L^{-1} området eller under, og i samsvar med data fra PBDE og spesielt PBDE 209 fra første utplassering. Reproduserbarheten var innenfor det forventede området. Konsentrasjonene av frie, oppløste PAH-forbindelser målt med de to forskjellige prøvetakerne var konsistente. I tillegg var konsentrasjonene av PCB og PBDE målt med LDPE-membraner i samsvar med funnene fra 2009. Suspendert partikulært materiale ble prøvetatt ved tre forskjellige anledninger med den kontinuerlige vannstrømssentrifugen for å måle konsentrasjonene av miljøgiftene. Dette ga data som kunne benyttes til å beregne fordelingskoeffisienten til suspendert partikulært materiale for noen miljøgifter, og disse verdiene var tilsvarende funn fra 2009. K_{POC}-verdierfra 2010 var i god overensstemmelse med data beregnet året før. I 2010 var det mulig å måle BDE209 både i den partikulære og den frie fasen ved bruk av LDPE-membraner.

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).

Both in 2008 and 2009, the Norwegian Climate and Pollution agency (Klif) commanded studies 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, 2]. Considering the complexity of riverine environments and the low 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 spot sampling [3, 4]. Most sampling methodologies tested during these studies 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, 2]. 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, 2]. The levels of both contaminants and SPM measured in 2008 were very low in the Drammen River and this rendered the use and comparison of data particularly challenging [1]. Promising techniques were further evaluated in 2009 in the Glomma River and included the deployment of different types of passive sampling devices and collection of suspended particulate matter using both continuous flow centrifugation and time-integrative suspended sediment samplers. These techniques were able to provide measurements of concentrations at very low levels as a result of high sampling rates for passive samplers and collection of large volumes of suspended particulate matter [1, 2].

The aim of the present study was to build on previous experience and evaluate previously-identified promising techniques for the measurement of trace contaminant concentrations in water. To this end, the River Glomma and the RID monitoring site in Sarpsborg were selected for this study. Objectives were to:

- Expose a new configuration for a passive sampling device (low density polyethylene membranes) using an alternative cage design in order to maximise sampling rates for PAHs, PCBs/OCs and PBDEs.
- Test the use silicone strips for the passive sampling measurement of hexabromocyclododecane (HBCD) dissolved in water.
- Evaluate the use of one ^{13}C-labelled stereoisomer of HBCD as a possible performance reference compound (PRC) to improve the reliability of the time-integrative measurement of HBCD using silicone strip sampler.
- Perform week-long sampling of suspended particulate matter using the continuous-flow centrifuge for the measurement of concentrations of PAHs, PCBs/OCs, PBDEs and HBCD.
- Understand contaminant partitioning between dissolved and particulate phases in the river Glomma.

Further objectives of this report include:

- Reviewing of data obtained throughout the RiverPOP projects conducted from 2008 to 2010.
- Propose (based on the review) a set of recommendation for the application and implementation of tools tested during these projects for monitoring programmes such as RID.

2. Material and methods

2.1 Fieldwork and study site description

The site chosen for this particular study is the RID programme monitoring site on the River Glomma in Sarpsborg near the mouth of the river (see Figure 1). 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 and the passive sampling devices. 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 passive sampling devices. However, deployment had to be moved to a second site further upstream as the channel was being serviced during the autumn.

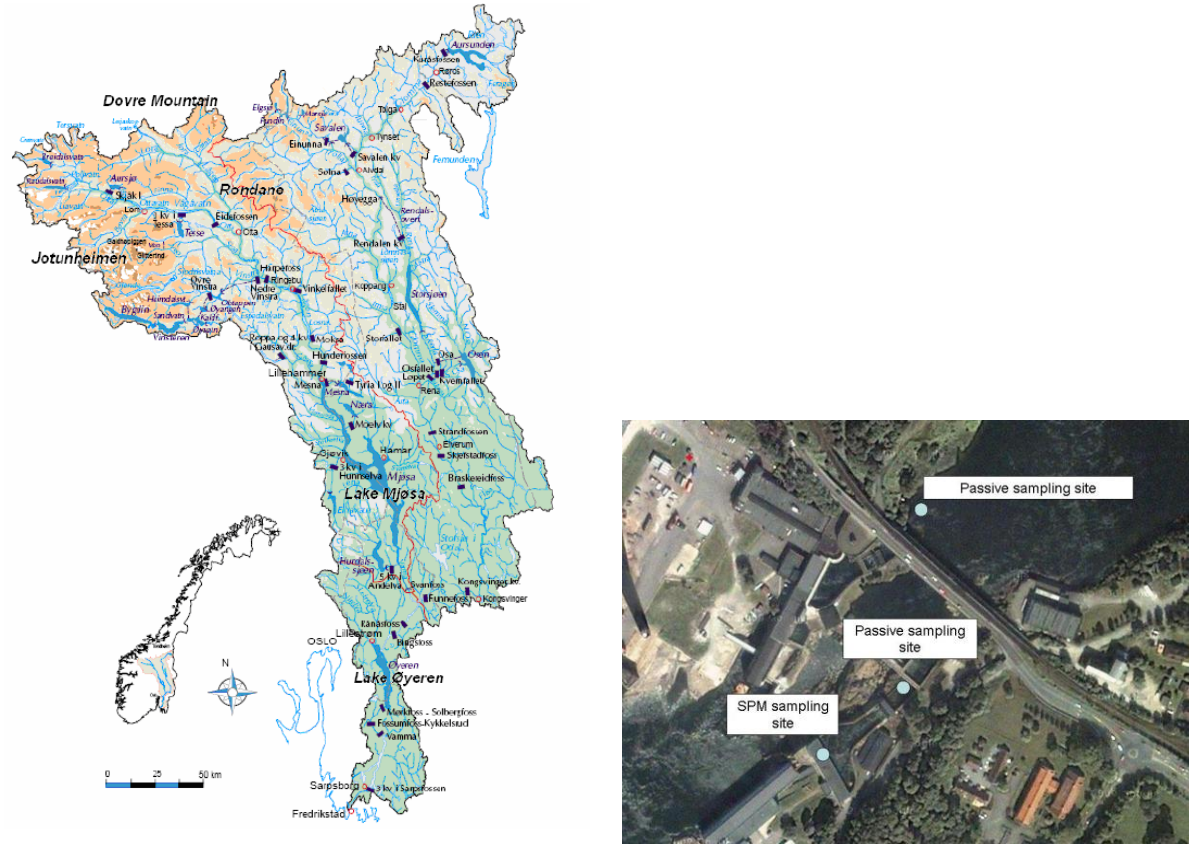

Figure 1. Map of the catchment area (from GLB annual report; www.glb.no) for the River Glomma (left) and passive sampling and suspended particulate matter (SPM) sampling sites in the River Glomma in Sarpsborg for 2010 (right).

2.2 Sampling of organic contaminants in the dissolved phase

2.2.1 Sampling of PAHs, PCBs/OCs and PBDEs with density polyethylene membranes

Low density polyethylene (LDPE) membranes were prepared from LDPE tubing purchased from Brentwoods Plastics (US). The lay-flat LDPE tubing was cut on one side only for the preparation of 5 cm wide (nominal) samplers. The length was adjusted to ~ 1 m for a final nominal surface area of 1000 cm^2. To ensure minimal contamination, samplers were left soaking overnight in pentane and hexane prior to a final rinse with methanol. Samplers were then spiked with a range of performance reference compounds (PRCs) following procedures previously developed and tested [5-8]. Once spiked, samplers were kept in the freezer at -20 °C until deployment. PRCs used here were acenaphthene-d_{10}, fluorene-d_{10}, phenanthrene-d_{10}, fluoranthene-d_{10}, chrysene-d_{12} and benzo[*a*]pyrene-d_{10}. The reproducibility in the preparation of the samplers is shown in Table 1. Samplers were deployed for three successive periods of four weeks as shown in Table 2.

Table 1. Nominal dimensions for LDPE membranes and silicone strips and masses of the samplers following extraction in the laboratory (+ standard deviation/ % RSD for n = 12)

	Nominal dimensions (cm)			Mass (g) (*sd*; *n*=12)	% RSD *(sd; n*=12)
	Length	Width	Thickness		
LDPE membranes	100	5	0.007	3.73 (*0.05*)	1.2
Silicone strips	100	2.5	0.05	18.5 (*0.6*)	3.4

2.2.2 Sampling for HBCD with silicone strips

Screening of extracts from silicone strips exposed in the Drammen River showed that α- and γ-HBCD could be consistently detected in the samplers but not in the trip control sampler. AlteSil® polydimethylsiloxane sheets were obtained from Altec Ltd (Cornwall, UK). Samplers, 100 cm long and 2.5 cm wide were produced from 0.05-cm thick sheets. Soxhlet extraction using a combination of acetone/hexane (50:50) was conducted to clean the sheets and remove possible silicone oligomers that may interfere with the chromatography. This step was repeated with fresh solvents. Samplers were then left to dry and were rinsed with methanol prior to spiking with PRCs. Since silicone strips were selected for the measurement of HBCD, one aim here was to evaluate the use of a ^{13}C-labelled stereoisomer of HBCD as PRC, the two remaining ones to be used as recovery standards during extraction of the exposed samplers. Similar PRCs as those used for LDPE membranes were spiked together with ^{13}C-labelled β-HBCD into silicone strips using a protocol previously described [5-8]. Once samplers spiked, these stored in clean tins in the freezer at -20 °C. The reproducibility in the preparation of the samplers is shown in Table 1. Samplers were deployed for three successive periods of four weeks as shown in Table 2.

Table 2. Deployment and retrieval dates for passive sampling devices exposed in the river Glomma in 2010

	Deployment date	Retrieval date	Exposure time (d)
Period 1	20/08/2010	17/09/2010	28
Period 2	17/09/2010	15/10/2010	28
Period 3	15/10/2010	12/11/2010	28

2.3 Sampling of organic contaminants associated with suspended particulate matter

The continuous-flow centrifuge was set-up for week-long continuous sampling once a month for the duration of the field test. The Hafslund AS site was also used for this sampling since it provided a secure site. Procedures previously described were also used here [1, 2]. The use of secure site made it possible to increase the sampling time to ~ 7 days allowing the collection of relatively high masses of SPM. In total three samples were collected. 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. Exact sampling dates and duration of the sampling are provided in the Table 3, below.

Table 3. Periods of sampling undertaken with the continuous-flow centrifuge for the river Glomma in 2010

	Deployment date	Retrieval date	Exposure time (d)
SPM 1	30/08/2010	03/09/2010	4
SPM 2	17/09/2010	24/09/2010	7
SPM 3	15/10/2010	22/10/2010	7

2.4 Extraction and analysis for organic contaminants

2.4.1 Passive sampling: Preparation and trip controls

The ISO standard (in development) on passive sampling of surface water provides recommendations regarding the number of trip and preparation controls to be used when using passive samplers. Trip controls associated with each sampling sites are recommended. A number of preparation controls is also needed to assess initial PRC concentrations. Since we did not expect significant contamination during deployment and retrieval procedures, we attempted to minimise the number of trip and preparation controls used here. Two trip controls and 1 preparation control were used for each type of samplers.

2.4.2 LDPE membrane extraction for PAHs, PCBs/OCs and PBDEs

All controls and exposed samplers were cleaned by ultra pure water and wiped with a clean tissue. Samplers were dialysed twice with 100 mL hexane (Rathburn, HPLC Grade, Scotland) for 24 hours and the extracts combined. Extracts were spiked with internal standards for PAHs; naphthalene-d_8, biphenyl- d_{10}, acenaphthylene-d_8, pyrene-d_{10} and perylene-$d_{12,}$ (Chiron AS, Norway), PBDEs; BDE -30, -119, -181 and -209^{13}C, (Cambridge Isoptope Laboratories, Inc, USA) and PCB/OCs; PCB- 29, -53 and -204 (Dr Ehrenstorfer GmbH -Germany). Hexane extracts were reduced under nitrogen (AGA 5.0 Norway) and split into two. The extracts for BDE determination were cleaned up with sulphuric acid (Merck, for analysis 95-97%, USA) before they were partitioned with acetonitrile (Rathburn, HPLC Grade, Scotland) and the acetonitrile portion quantitatively removed and reduced prior to analysis. The second extracts were cleaned up by gel permeation chromatography. The system consists of two serial couplets Envirogel^{TM} GPC-clean up column, 19x300mm and 19x150mm (Waters, Sweden). This extract was split whereas one extract was reduced under nitrogen before PAH analysis and the other extracts were cleaned up with sulphuric acid before reduction under nitrogen and PCBs/OCs analysis.

2.4.3 Silicone strip extraction for PAHs and HBCD

The same procedure was used as for LDPE. However, methanol (Rathburn, HPLC grade) was used as solvent instead of hexane. Extracts were spiked with internal standards for PAHs (the same as for LDPEs) and HBCD; α- and γ-HBCD^{13}C, (Cambridge Isoptope Laboratories, Inc, USA). First the

solvent was exchanged from methanol to iso-hexane (Riedel-Detlaën, Pestanal, Germany) before the extracts where split. Extracts for PAH analysis were cleaned as described for LDPEs. The other extract was cleaned up with sulphuric acid before the solvents were exchanged to acetonitrile/water in preparation of HBCD determination

2.4.4 Extraction and analysis of suspended particulate matter for PAHs, PCBs/OCs, PBDEs and HBCD

Internal standard for PAHs, PCB/OCs, PBDEs and HBCDs were added to freeze-dried SPM samples before they were extracted with dichloromethane (Rathburn, HPLC Grade, Scotland). The internal standards added where the same as those used for the passive samplers, except for PAHs where acenaphthene-d_8, phenanthrene-d_{10} and chrysene-d_{12} (Chiron AS, Norway) were also added. The extracts were split into a total of four extracts and the clean up procedures were performed as described for the passive samplers for the different compound groups.

2.4.5 Analysis for PAHs, PCBs/OCs, PBDEs and HBCD

PAH analysis: Extracts were analysed used a HP-6890N gas chromatograph (GC) equipped with a HP 5973 Mass Selective Detector (MS) (Agilent Technologies, USA) operated in single ion monitoring mode (SIM) with electron impact ionisation (70 eV). The identification was made by comparing retention times and specific ions for each compound in standard solutions and sample extracts. Quantification was performed with both internal and external standards. Analytes were separated on a 30 m DB-5 column (0,25 mm i.d. and 0.25 µm film) (Agilent Technologies, USA)and with a helium (AGA 6,0 Norway) flow of 1 mL min^{-1}. The temperature was held for 2 min at 60 °C before ramping to 250 °C at a rate of 7 °C min^{-1}. The final step was an increase to 310 °C at a rate of 15 °C min^{-1} (held for 6 min). The injector, transfer line, ion source and quadruple temperatures were set to 280, 280, 230 and 150 °C, respectively.

PCB/OC analysis: Extracts were analysed by Agilent 6890N gas chromatograph (GC) equipped with a G2397A micro Electron Capture detector (µECD) (Agilent Technologies, USA). The identification was made by comparing retention times in standard solutions and sample extracts. The quantification was performed with both internal and external standards. Analytes were separated on a 60 m DB-5 column (0,25 mm i.d. and 0.25 µm film) (Agilent Technologies, USA) . The temperature was held for 2 min at 90 °C before ramping to 180 °C at a rate of 10 °C min^{-1}. The final two steps were increases to 270 °C then to 310 °C at rates of 2 °C and 20 °C min^{-1}, respectively (held for 6 min). The injector and detector temperatures were set to 255 and 285 °C, respectively.

PBDE analysis: Extracts were analysed used a HP-6890 gas chromatograph (GC) equipped with a HP 5973 Mass Selective Detector (MS) (Agilent Technologies, USA) operated in single ion monitoring mode (SIM) with negative chemical ionisation (NCI) and methane (AGA 4,0 Norway) as the reagent gas. The identification was made by comparing retention times and characteristic ions (486/488 for BDE-209 and 79/81 for all other analytes) in standard solutions and sample extracts. The quantification was performed with both internal and external standards. Pulsed splitless injection was used to introduce samples onto a 15 m DB-5MS (0,25 mm i.d. and 0,10 µm film) (Agilent Technologies, USA). The temperature was held for 2 min at 120 °C before ramping to 180 °C at a rate of 25 °C min^{-1}. The final two steps were increase to 250 °C then to 345 °C at rates of 15 °C and 25 °C min^{-1} respectively (held for 5 min). The flow was kept at 1.1 mL min^{-1}. The injector, transfer line, ion source and quadrupole temperatures were set to 280, 325, 250 and 150 °C, respectively.

HBCD analysis: Liquid chromatography – mass spectrometry (LC/MS/MS) analysis used a Waters Aquity UPLC coupled to a Waters Quattro Premier XE triple quadruple mass spectrometer (Micromass, Sweden). Analytes were separated on an Aquity BEH C_{18} 1.7 µm column (2.1 x 50 mm)

(Waters, Sweden). The mobile phases for optimised separation were water/methanol (70/30) and acetonitrile/methanol (70/30) using a gradient elution programme starting with 100% water/methanol and finishing with 100% acetonitrile/methanol at a flow rate of 0.4 ml min^{-1}. Standards (1 µg mL^{-1}) were made in acetonitrile and directly infused into the MS to optimise MS parameters. The capillary was set to 3.2 kV, the source temperature 100 ^{o}C and the desolvation temperature 350 ^{o}C. The nitrogen cone gas was at a flow rate of 50 L h^{-1} and the argon desolvation gas at 900 L h^{-1} with cone and collision voltages of 15 V and 30 V respectively. Two MRM transitions were used for each isomer 640.6 → 78.9/80.9.

3. Results and discussion

3.1 Sampling rates of passive samplers

Sampling rates can generally be estimated from the release rate of PRCs from passive samplers during exposure [4, 9]. A number of PRCs were spiked both in LDPE membranes and silicone strips. The reproducibility was checked by analysing 2 trip control samplers as well as 4 (3 for silicone strips) preparation control devices.

Sampling rates R_s (L d^{-1}) were calculated from PRC dissipation rates k_e (d^{-1}), the sampler mass m_s (g) and the sampler-water partition coefficient K_{sw} (mL g^{-1}) for the PRC of interest:

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

An expected low variability in the PRC spike of LDPE membranes was observed for acenaphthene-d_{10} and fluorene-d_{10} (4.5 and 8.2 % relative standard deviation, respectively). For phenanthrene-d_{10} this was approximately 13 % and higher for the other higher molecular weight PRCs which renders the data difficult to analyse. For silicone strips, the data was more variable and the relative standard deviation of PRC levels in control samplers were in the range 30-90 % which is surprisingly high. We do not at present understand the reasons for these data. It is possible that the exposure time during spiking was not sufficiently long to enable homogenous distribution of the PRCs throughout the batch of samplers. All other batches of samplers produced using this protocol showed adequate levels of reproducibility.

For LDPE membranes, the fraction remaining in the samplers for acenaphthene-d_{10} and fluorene-d_{10} for was very close to the analytical limits of detection on the GC/MS and the data are therefore not useable. Median sampling rates were estimated from phenanthrene-d_{10} and fluoranthene-d_{10} for triplicate samplers from each exposure period. Values are provided in Tables 4 and 5.

Table 4. Sampling rates R_s for LDPE membranes exposed for three consecutive 28 day periods in the River Glomma in 2010

	Sampling rates, R_s (L d^{-1}), (SD; n=3)		
	Exposure 1	Exposure 2	Exposure 3
Acenaphthene-d_{10}	(A)	(A)	(A)
Fluorene-d_{10}	(A)	(A)	(A)
Phenanthrene-d_{10}	**75***	**55***	**24***
Fluoranthene-d_{10}			
Chrysene-d_{12}	(B)	(B)	(B)
Benzo[*a*]pyrene-d_{10}	(B)	(B)	(B)

(A): PRC mass remaining < 0.5 %
(B): High variability of PRC spike measured in 2 trip control and 4 preparation control samplers
*Median value estimated from data for phenanthrene-d_{10} and fluoranthene-d_{10} from triplicate samplers

Table 5. Sampling rates R_s for silicone strips exposed for three consecutive 28 day periods in the River Glomma in 2010

	Sampling rates, R_s (L d^{-1}), (SD; n=3)		
	Exposure 1	Exposure 2	Exposure 3
Acenaphthene-d_{10}	(A)	(A)	(A)
Fluorene-d_{10}	(A)	(A)	(A)
Phenanthrene-d_{10}			
Fluoranthene-d_{10}	**16***	**17***	**10***
Chrysene-d_{12}	(A)	(A)	(A)
Benzo[a]pyrene-d_{10}	(A)	(A)	(A)
(A): High variability of PRC spike measured in 2 trip control and 3 preparation control samplers *Median value estimated from data for phenanthrene-d_{10} and fluoranthene-d_{10} from triplicate samplers			

According to the tables above, sampling rates appeared to be the lowest during Exposure 3 for both types of samplers. Sampling rates appeared higher for Exposure 1 than for Exposure 2 for LDPE membranes, while for silicone strips these were similar. These differences can easily be the result of differences in turbulences around the samplers, biofouling or simply a radical drop in temperature of the water in the Glomma River between August and November 2010. Sampling rates were substantially higher for LDPE membranes than for silicone strips. This is not surprising as the surface area of LDPE membrane samplers was almost twice as high as that of silicone strips.

The spiking of ^{13}C-labelled β-HBCD into silicone strips using the method used for standard PRCs was tentatively tested here. Recoveries based on the nominal concentration of the spiking solution were low and spiking levels were found to be variable (Figure 2). While the variation for exposed samplers appears smaller than for control samplers, this is the result of one high value for a control sampler. Median values for control and exposed samplers are in a similar range. Overall, this indicates that (i) this method has the potential to work, (ii) more work is needed to develop and optimise a suitable approach for the use of ^{13}C-labelled β-HBCD as a PRC (ii) this data cannot be used at present to establish sampling rates for HBCD isomers.

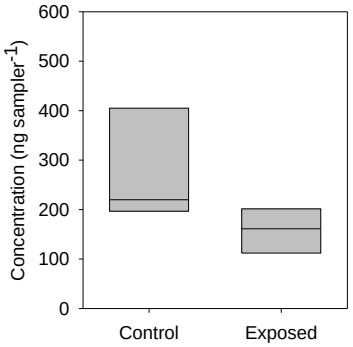

Figure 2. Distribution of masses of ^{13}C-labelled β-HBCD in control samplers (preparation and trip controls, n= 6) and in exposed samplers (n=8)

Time-weighted average concentrations were calculated using the following equation:

$$C_w = \frac{m}{K_{sw} m_s (1 - e^{-\frac{R_s}{K_{sw} m_s} t})}$$

where m is the mass of contaminant accumulated in the sampler (ng), K_{sw} the sampler-water partition coefficient (mL g^{-1}), m_S the mass of the sampler (g), t the exposure time (d) and R_S the uptake rate (L d

[1]). 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 (based on the median value from deuterated phenanthrene and fluoranthene) was found to be the simplest method here. A similar methodology was employed for data from the 2009 study in the Glomma [2]. 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.

3.2 Dissolved PAHs in the river Glomma

PAHs were detected both in extracts from LDPE membrane and silicone strip samplers. Trip control and preparation control samplers contained negligible levels of PAHs. Silicone strip controls had on average 44 ng of naphthalene and 9 ng of phenanthrene and one sampler had levels of fluorene above limits of detection (6.7 ng sampler^{-1}). For LDPE membranes, all analytes were below limits of detection. Masses absorbed by triplicate LDPE membranes for three consecutive exposures of 28 days are given in Table 6. Those found in silicone strips are presented in Table 7. Naphthalene concentrations in LDPE samplers were below limits of detection, as were those for benzo[*a*]pyrene, indeno[*1,2,3-cd*]pyrene and dibenzo[*a,h*]anthracene. Compounds below limits of detection were mostly the same for silicone strip samplers as those for LDPE membranes. Silicone strips allowed the absorption of masses of naphthalene > 3x levels in the control samplers for Exposures 2 and 3. Benzo[*k*]fluoranthene was below limits of detection with silicone strips. For LDPE membranes, the median of relative standard deviations (%) for all compounds above limits of detection was 7.1 (range of 0.5 to 23.2 %). For silicone strips, the median was 7.9 and the range of relative standard deviation was 0.4-60.7 %. This is slightly higher than for LDPE membranes. Highest relative standard deviations were observed for compounds with log K_{ow} < 5. The reproducibility of these measurements is in line with previously obtained data [1, 2, 5, 6, 9].

Table 6. Masses of PAHs absorbed by LDPE membranes exposed during three periods in the River Glomma from Sept-Nov 2010

	Mass absorbed (ng sampler^{-1}) (SD, n=3)					
	Exposure 1		Exposure 2		Exposure 3	
	Mean	SD	Mean	SD	Mean	SD
ACY	<5		<5		<5	
ACE	**7.2**	**0.9**	**9.8**	**1.8**	**12.8**	**0.7**
FLUE	**6.9**	**0.7**	**16.2**	**2.6**	**23.6**	**1.8**
DBTHIO	<5		**6.5**	**1.0**	**6.6**	**1.4**
PHE	**61**	**7**	**129**	**28**	**190**	**20**
ANT	<5		**6.5**	**1.5**	**8.9**	**0.8**
FLUO	**119**	**1**	**221**	**4**	**264**	**26**
PYR	**86**	**1**	**152**	**4**	**190**	**19**
B*a*A	**10.1**	**0.2**	**14.3**	**0.3**	**21.8**	**4.4**
CHRY	**18.9**	**1.0**	**27.6**	**0.9**	**38.7**	**2.9**
B*bj*F	**25.0**	**0.3**	**23.9**	**0.6**	**26.8**	**1.9**
B*k*F	**5.0**	**0.0**	**5.3**	**0.2**	**6.1**	**0.6**
B*e*P	**14.5**	**0.4**	**12.0**	**0.5**	**12.2**	**1.1**
B*a*P	<5		<5		<5	
PeR	**30.6**	**0.5**	**16.6**	**0.5**	**9.7**	**0.1**
In*123cd*P	<5		<5		<5	
DB*ah*A	<5		<5		<5	
B*ghi*P	**5.5**	**0.4**	5.2*		5.3**	

*only detected in one sampler
**only detected in two samplers

Table 7. Masses of PAHs absorbed by silicone strips exposed during three periods in the River Glomma from Sept-Nov 2010

	Mass absorbed (ng sampler^{-1})					
	Exposure 1		Exposure 2		Exposure 3	
	Mean	SD	Mean	SD	Mean	SD
NAP	(A)	(A)	**119**	**7**	**186**	**6**
ACY	**16**	**2**	**28**	**2**	**73**	**1**
ACE	**85**	**48**	**73**	**18**	**135**	**6**
FLUE	**111**	**59**	**188**	**59**	**348**	**40**
DBTHIO	**25**	**15**	**39**	**15**	**49**	**9**
PHE	**645**	**339**	**879**	**311**	**1303**	**218**
ANT	**25**	**10**	**33**	**11**	**49**	**8**
FLUO	**216**	**1**	**242**	**15**	**293**	**11**
PYR	**118**	**2**	**135**	**8**	**173**	**6**
B*a*A	**10.2**	**1.5**	**13.6**	**0.8**	**17.1**	**0.4**
CHRY	**14.1**	**1.4**	**17.8**	**2.4**	**24.9**	**1.6**
B*bj*F	**14.4**	**1.1**	**16.2**	**2.7**	**17.3**	**0.6**
B*k*F	<5		<5		**15****	
B*e*P	**7.4**	**0.6**	**7.2**	**1.2**	**7.3**	**0.1**
B*a*P	<5		<5		<5	
PeR	**16.5**	**0.9**	**10.6**	**0.7**	**5.6**	**0.1**
In*123cd*P	<5		<5		<5	
DB*ah*A	<5		<5		<5	
B*ghi*P	<5		<5		<5	

(A): Values close to levels found in control samplers
*Detected in one sampler only

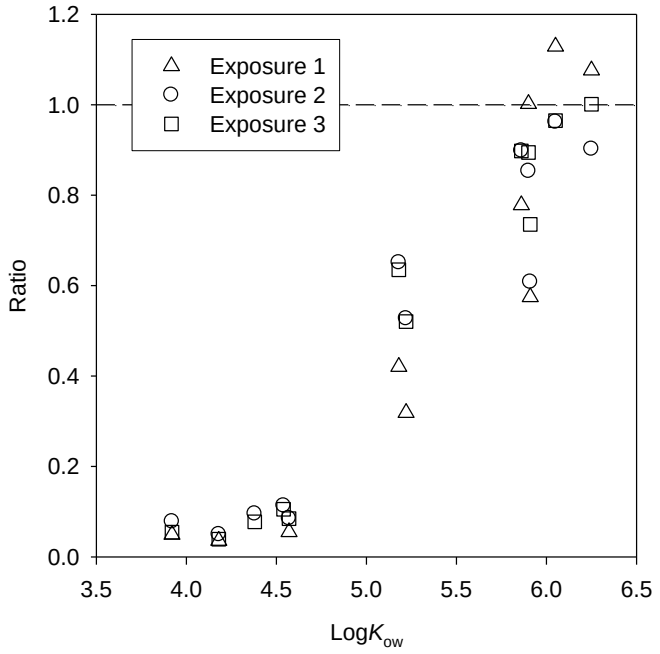

Figure 3. Ratio of masses of PAHs (normalised to sampler surface area) absorbed by LDPE membranes over those absorbed in silicone strips for the three consecutive passive sampler exposures

The masses of PAHs absorbed by the different types of passive samplers can be compared by plotting ratio of masses normalised to the surface area of the respective samplers (Figure 3). Normalisation was

necessary since LDPE membranes were twice the size of silicone strips. A ratio of 1 is expected if the uptake is boundary layer controlled and if sampling for both types of samplers remains integrative. A $m_{LDPE}/m_{Silicone} < 1$ is expected for compounds closer to equilibrium as a result of the much larger volume of the silicone strips [5, 6, 9, 10]. Ratios appear to drop below 0.8-1 for analytes with log K_{ow} ~ 5.7-5.9 (See Figure 3).

Dissolved concentrations were calculated from masses accumulated and sampling rates given in the previous section and are presented in the Tables below. Tables 8 and 9 present dissolved PAH concentrations measured with LDPE membranes and silicone strips, respectively. Dissolved concentrations for the three consecutive exposures are given. Concentrations are found to be in the low ng L^{-1} range for low molecular weight and around /below 10 pg L^{-1} for higher molecular weight PAHs. While most PAH concentrations were above limits of detection, concentrations of highest molecular weight PAHs below limits of detection were likely to be < 10-20 pg L^{-1} according to both LDPE membrane and silicon strip samplers.

Table 8. Concentration of PAHs measured with LDPE membranes exposed during three periods in the River Glomma from Sept-Nov 2010

	C_w (ng L^{-1}) (SD, n=3)					
	Exposure 1		Exposure 2		Exposure 3	
	Mean	SD	Mean	SD	Mean	SD
NAP	<8		<8		<8	
ACY	<0.5		<0.5		<0.5	
ACE	**0.86**	**0.10**	**1.2**	**0.2**	**1.5**	**0.1**
FLUE	**0.34**	**0.04**	**0.8**	**0.2**	**1.2**	**0.1**
DBTHIO	<0.1		**0.16**	**0.03**	**0.16**	**0.04**
PHE	**0.80**	**0.09**	**1.7**	**0.4**	**2.5**	**0.3**
ANT	<0.1		**0.09**	**0.02**	**0.13**	**0.01**
FLUO	**0.18**	**0.01**	**0.35**	**0.01**	**0.61**	**0.06**
PYR	**0.15**	**0.01**	**0.27**	**0.01**	**0.47**	**0.05**
B*a*A	**0.006**	**0.001**	**0.010**	**0.001**	**0.034**	**0.007**
CHRY	**0.011**	**0.001**	**0.020**	**0.001**	**0.06**	**0.01**
B*bj*F	**0.014**	**0.001**	**0.017**	**0.001**	**0.042**	**0.003**
B*k*F	**0.003**	**0.001**	**0.004**	**0.001**	**0.009**	**0.001**
B*e*P	**0.008**	**0.001**	**0.008**	**0.001**	**0.019**	**0.002**
B*a*P	<0.003		<0.003		<0.008	
PeR	**0.015**	**0.001**	**0.011**	**0.001**	**0.015**	**0.001**
In*123cd*P	<0.002		<0.003		<0.008	
DB*ah*A	<0.002		<0.003		<0.007	
B*ghi*P	**0.003**	**0.001**	**0.003***		**0.008****	

*only detected in one sampler
**only detected in two samplers

Table 9. Concentration of PAHs measured with silicone strips exposed during three periods in the River Glomma from Sept-Nov 2010

	C_w (ng L^{-1})					
	Exposure 1		Exposure 2		Exposure 3	
	Mean	SD	Mean	SD	Mean	SD
NAP	**3.3***	**1.5**	**7.8**	**0.5**	**12.2**	**0.4**
ACY	**0.26**	**0.03**	**0.44**	**0.02**	**1.15**	**0.01**
ACE	**1.6**	**0.9**	**1.4**	**0.3**	**2.5**	**0.1**
FLUE	**1.2**	**0.6**	**2.0**	**0.6**	**3.8**	**0.4**
DBTHIO	**0.17**	**0.10**	**0.27**	**0.10**	**0.38**	**0.07**
PHE	**3.2**	**1.7**	**4.3**	**1.5**	**7.8**	**1.3**
ANT	**0.13**	**0.05**	**0.17**	**0.06**	**0.30**	**0.05**
FLUO	**0.59**	**0.01**	**0.64**	**0.04**	**1.16**	**0.04**
PYR	**0.33**	**0.01**	**0.37**	**0.02**	**0.70**	**0.03**
B*a*A	**0.024**	**0.003**	**0.031**	**0.002**	**0.061**	**0.001**
CHRY	**0.033**	**0.003**	**0.040**	**0.005**	**0.089**	**0.006**
B*bj*F	**0.034**	**0.002**	**0.036**	**0.006**	**0.062**	**0.002**
B*k*F	<0.01		<0.01		**0.053****	
B*e*P	**0.018**	**0.001**	**0.016**	**0.003**	**0.026**	**0.001**
B*a*P	<0.01		<0.01		<0.02	
PeR	**0.037**	**0.002**	**0.023**	**0.001**	**0.020**	**0.001**
In*123cd*P	<0.01		<0.01		<0.02	
DB*ah*A	<0.01		<0.01		<0.02	
B*ghi*P	<0.01		<0.01		<0.02	
*Value close to levels found in control samplers **Detected in only one sampler						

Figure 4 presents a comparison of dissolved PAH concentrations measured with silicone strips (x-axis) and LDPE (y-axis) for the three consecutive exposures in the River Glomma. Further data for measurements undertaken in 2009 are also plotted [2]. Most data points tend to be below the 1:1 relationship which indicates that concentrations estimated with LDPE membranes are generally higher than those from silicone strips. Data from the 2009 confirms this. These differences can be the result of a number of processes. These can involve differences in biofouling of the samplers or the estimation of sampling rates, given the particularly high variability of the PRC data for these two batches of samplers. It is possible that the uncertainty in sampler-water partition coefficients contributes significantly to these differences [4, 8, 9]. Differences appear to amount to no more than a factor of two which is good considering the possible sources of uncertainty.

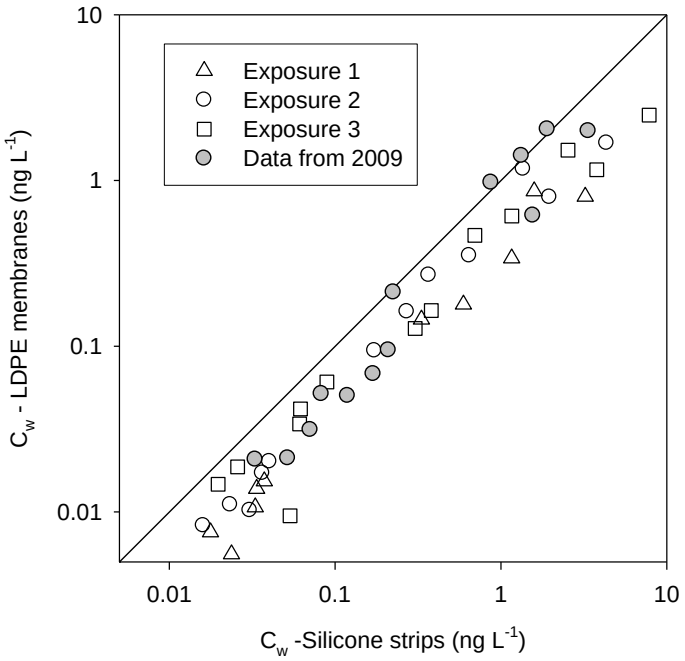

Figure 4. PAH concentrations measured with LDPE membranes and silicone strips in the River Glomma for three exposures in 2010 and with a comparison with data from 2009. Note the log scale.

3.3 Dissolved PCBs/OCs in the river Glomma

Extracts from LDPE membrane samplers were split and a fraction was cleaned up and analysed for PCBs and some organochlorines (OCs). Masses of PCBs and OCs detected in the extracts are given in Table 10. CB153 was the only PCB found in LDPE membranes above limits of detection. Pentachlorobenzene (PeCB) was only found above limits of detection in extracts from samplers from Exposures 2 and 3. HCB was consistently detected in all replicate LDPE membranes from all three exposures. DDT transformation product, *p,p'*-DDE was also found above limits of detection in all exposed samplers. The reproducibility of the measurements of masses of PCBs and OCs was high and the relative standard deviations of triplicate measurements were in most cases < 10 % (higher for CB153).

Table 10. Masses of PCBs/OCs absorbed by LDPE membranes exposed during three periods in the River Glomma from Sept-Nov 2010

	Mass absorbed (ng $sampler^{-1}$)					
	Exposure 1		Exposure 2		Exposure 3	
	Mean	SD	Mean	SD	Mean	SD
CB28	<1		<1		<1	
CB52	<1		<1		<1	
CB101	(A)		(A)		(A)	
CB118	<1		<1		<1	
CB105	<1		<1		<1	
CB153	**2.3**	**1.0**	**1.3**	**0.2**	**1.60***	
CB138	<1		<1		<1	
CB156	<1		<1		<1	
CB180	<1		<1		<1	
CB209	<1		<1		<1	

PeCB	<0.5		**0.64**	**0.09**	**0.88**	**0.03**
α-HCH	<1		<1		<1	
HCB	**6.2**	**0.5**	**7.3**	**0.3**	**8.8**	**0.2**
γ-HCH	<2		<2		<2	
p,p'-DDE	**2.7**	**0.1**	**2.3**	**0.1**	**2.13**	**0.2**
P,p'-DDD	<2		<2		<2	
(A) interferences on the GC/ECD chromatogram *Only detected in 1 sampler						

Resulting concentrations were calculated using sampling rates as explained previously and are presented in Table 11. Considering the relatively high sampling rates found for these exposures and the masses accumulated generally close to analytical limits of detection, it is not surprising to observed very low concentrations dissolved in water. Dissolved CB153 concentrations appear to be in the range 1-2 pg L^{-1} while those for PeCB and *p,p'*-DDE are found to be in a similar range (1-5 pg L^{-1}). HCB concentrations were roughly one order of magnitude higher than that.

Table 11. Concentration of PCBs/OCs measured with LDPE membranes exposed during three periods in the River Glomma from Sept-Nov 2010

	C_w (ng L^{-1})					
	Exposure 1		Exposure 2		Exposure 3	
	Mean	SD	Mean	SD	Mean	SD
CB28	<0.001		<0.001		<0.002	
CB52	<0.001		<0.001		<0.002	
CB101	(A)		(A)		(A)	
CB118	<0.001		<0.001		<0.002	
CB105	<0.001		<0.001		<0.002	
CB153	**0.0011**	**0.0005**	**0.0009**	**0.0001**	**0.0024***	
CB138	<0.001		0.001		<0.002	
CB156	<0.0005		0.001		<0.002	
CB180	<0.0005		0.001		<0.001	
CB209	<0.0005		0.001		<0.001	
PeCB	<0.002		**0.0024**	**0.0003**	**0.0036**	**0.0001**
α-HCH	<0.2		<0.2		<0.2	
HCB	**0.010**	**0.001**	**0.013**	**0.001**	**0.021**	**0.001**
γ-HCH	<0.4		<0.4		<0.4	
p,p'-DDE	**0.0029**	**0.0001**	**0.0028**	**0.0001**	**0.0043**	**0.0002**
p,p'-DDD	<0.001		<0.002		<0.003	
(A) interferences on the GC/ECD chromatogram *Only detected in 1 sampler						

A comparison of concentrations of PCBs/OCs from the three exposures and with data from the study conducted in 2009 (Figure 5) shows slightly higher concentrations for the last exposure period when compared with the other two. Concentrations measured in 2010 are generally in line with those measured the previous year. Concentrations of PCBs/OCs are consistently below limits of detection when bottle sampling as part of the RID monitoring is used. Limits of detection acheieved here are close to 3 orders of magnitude below those from bottle sampling.

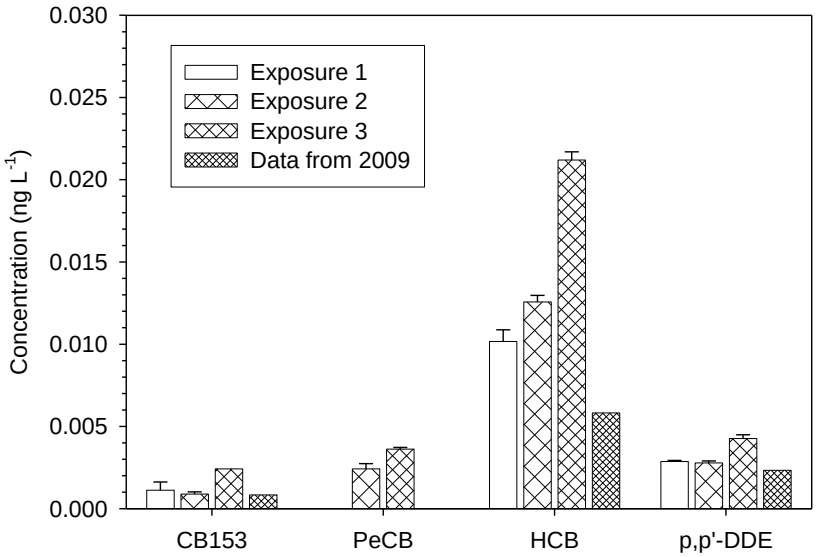

Figure 5. Comparison of concentrations of CB153, pentachlorobenzene (PeCB), hexachlorobenzene (HCB) and *p,p'*-DDE measured in the River Glomma with LDPE membranes in 2010 (three exposures) and in 2009

3.4 Dissolved PBDEs in the river Glomma

PBDE masses accumulated in the LDPE membrane samplers are given in Table 12. Most brominated flame retardants were below limits of detection. Only BDE47, 99 and 209 were detected. BDE47 was consistently detected throughout the deployments, while BDE99 and 209 were only detected in extracts from samplers exposed during the first deployment. The variability in masses accumulated for the different congeners were low (< 10 % relative standard deviation). One trip control samplers presented a concentration of BDE209 above limits of detection (~ 1.4 ng sampler^{-1}). However BDE209 was only consistently found in samplers exposed during the first deployment. This together with a low variability tends to indicate that this measurement is genuine.

Table 12. Masses of PBDEs absorbed by LDPE membranes exposed during three periods in the River Glomma from Sept-Nov 2010

	Mass absorbed (ng sampler^{-1})					
	Exposure 1		Exposure 2		Exposure 3	
	Mean	SD	Mean	SD	Mean	SD
BDE28	<0.2		<0.2		<0.2	
BDE47	**1.4**	**0.1**	**1.0**	**0.1**	**0.7**	**0.2**
BDE49	<0.5		<0.5		<0.5	
BDE66	<0.5		<0.5		<0.5	
BDE71	<0.5		<0.5		<0.5	
BDE85	<0.5		<0.5		<0.5	
BDE99	**0.24**	**0.02**	<0.1		<0.1	
BDE100	<0.2		<0.2		<0.2	
BDE138	<0.5		<0.5		<0.5	
BDE153	<0.2		<0.2		<0.2	
BDE154	<0.2		<0.2		<0.2	

BDE183	<0.5		<0.5		<0.5	
BDE196	<0.5		<0.5		<0.5	
BDE205	<0.5		<0.5		<0.5	
BDE209	**2.3**	**0.2**	<0.5		<0.5	

Resulting concentrations of PBDEs detected in LDPE samplers were calculated and these are presented in Table 13. All concentrations are close or below 1 pg L^{-1}. Field limits of detections were below 1 pg L^{-1}.

Table 13. Concentration of PBDEs measured with LDPE membranes exposed during three periods in the River Glomma from Sept-Nov 2010

	C_w (pg L^{-1})					
	Exposure 1		Exposure 2		Exposure 3	
	Mean	SD	Mean	SD	Mean	SD
BDE28	<0.1		<0.2		<0.3	
BDE47	**0.71**	**0.03**	**0.65**	**0.04**	**1.04**	**0.24**
BDE49	<0.3		<0.3		<0.8	
BDE66	<0.3		<0.3		<0.8	
BDE71	<0.3		<0.3		<0.8	
BDE85	<0.2		<0.3		<0.7	
BDE99	**0.12**	**0.03**	<0.1		<0.1	
BDE100	<0.1		<0.1		<0.3	
BDE138	<0.2		<0.3		<0.7	
BDE153	<0.1		<0.1		<0.3	
BDE154	<0.1		<0.1		<0.3	
BDE183	<0.2		<0.3		<0.7	
BDE196	<0.2		<0.3		<0.7	
BDE205	<0.2		<0.3		<0.7	
BDE209	**1.12**	**0.10**	<0.3		<0.7	

The comparison of PBDE concentrations measured in the present study with data from the study conducted in 2009 was undertaken and is presented in Figure 6. BDE47 concentrations measured in 2009 are very close to those measured in 2010. The BDE99 concentration was slightly lower in 2010 compared with values from 2009. BDE209 concentrations were below limits of detection in samplers exposed in 2009 while those data from Exposure 1 in 2010 result in the quantification of BDE209 with a concentration close to 1 pg L^{-1}. Concentrations of PBDEs detected and quantified here are lower than those found for PCBs, while limits of detection are also an order of magnitude lower than those obtained for PCBs.

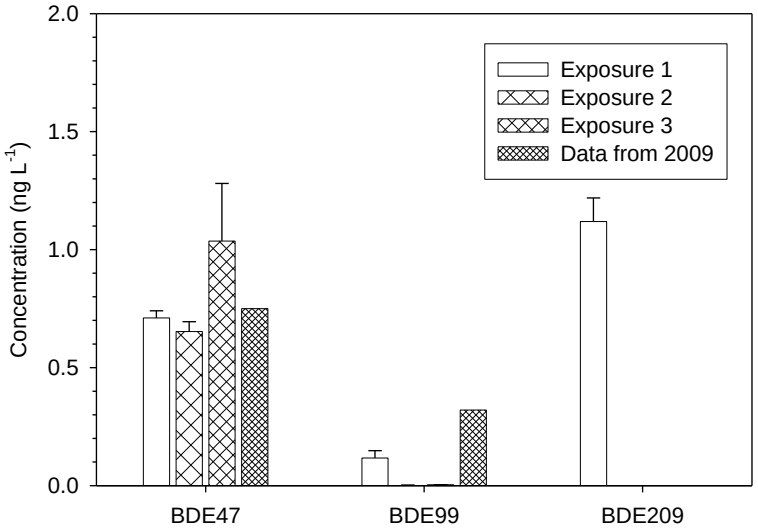

Figure 6. Comparison of concentrations of BDE47, BDE99, and BDE209 measured in the River Glomma with LDPE membranes in 2010 (three exposures) and in 2009

3.5 Dissolved HBCD in the river Glomma

The α-isomer of HBCD was relatively consistently detected in silicone strips exposed in the River Glomma (Table 14). β-HBCD was found in one sampler from Exposure 1, while remaining data were below limits of detection. This supports our assumption that passive sampling for HBCD isomers is possible; however this is likely to require substantially more development work in the laboratory.

Table 14. Masses of HBCD isomers found in silicone strip samplers following Exposure 1, 2 and 3 in the River Glomma

Exposure	Replicate	Mass accumulated (ng sampler^{-1})		
		α-HBCD	β-HBCD	γ-HBCD
1	1	**0.59**	**0.28**	<0.2
	2	<2	<0.5	<1.2
	3	**0.44**	<0.3	<0.2
2	1	**0.84**	<0.3	<0.2
	2	**0.79**	<0.3	<0.2
	3	**0.37**	<0.3	<0.2
3	1	**0.59**	<0.3	<0.2
	2	<0.2	<0.3	<0.2
	3	(A)	(A)	(A)
(A) broken vial				

3.6 Organic contaminant partitioning in the river Glomma

3.6.1 Contaminant concentrations in SPM

The continuous-flow centrifuge was used on three occasions to collect samples of suspended particulate matter (SPM) in the Glomma River. SPM samples were approximately 10 g dry weight or more after freeze drying. These amounts of samples were sufficient for all the analyses that were planned.

Table 15 present concentrations of PAHs associated with SPM measured on these three occasions. Concentrations measured during the first two sampling periods (30/08-03/09 and 17/09-24/09) were relatively low and below limits of detection for some PAHs. For others, concentrations were between a factor of 1 and 20 above the limit of detection of 2 ng g^{-1} dry weight of SPM. Concentrations are in the same range as those measured in SPM samples collected with the centrifuge and the time-integrative SPM samplers in 2009 [2]. The final sample was collected during the period 15/10-22/10 and exhibit PAH concentrations significantly higher than those measured in samples SPM 1 and 2 (Table 15). Concentrations increased by a factor of 2-100 when compared with samples SPM 1 and 2. While this is interesting, it is difficult to be certain whether these concentrations are real or whether this may be a result of possible contamination from activities/refurbishment activities taking place in the hall the centrifuge was set in this autumn. However, based on the working principle of the centrifuge it would be surprising to observe such a contamination from the surrounding air. In addition, all parts in contact with the water (i.e. the sample) including the centrifuge bowl are thoroughly solvent rinsed. Ideally, sampling should be repeated to establish whether this is real or a sampling artefact.

Table 15. Concentration of PAHs associated with suspended particulate matter (SPM) for three samples collected during Sept-Nov 2010 in the River Glomma

	C_{SPM} (µg kg^{-1} dry weight)		
	SPM 1	SPM 2	SPM 3
ACY	<2	<2	**4.3**
ACE	<2	<2	**40**
FLUE	**2.6**	<2	**40**
DBTHIO	<2	<2	**58**
PHE	**16**	**6.9**	**730**
ANT	<2	<2	**24**
FLUO	**22**	**12**	**880**
PYR	**18**	**9.9**	**620**
B*a*A	**5.6**	**2.9**	**230**
CHRY	**10**	**7.5**	**220**
B*bj*F	**17**	**13**	**320**
B*k*F	**5.9**	**3.6**	**110**
B*e*P	**8.4**	**6.1**	**150**
B*a*P	**5.6**	**3.4**	**150**
PeR	**39**	**22**	**75**
In*123cd*P	**5.3**	**3.5**	**86**
DB*ah*A	<2	<2	**24**
B*ghi*P	**6.7**	**4.3**	**95**

Table 16 present concentrations of PCBs and other organochlorines associated with SPM. Most PCBs were below the limit of detection of 0.5 ng g^{-1} dry weight of SPM. CB28 was found above limits of detection in samples SPM 2 and 3. CB153 was only detected in SPM 3 and the concentration similar

to that measured in 2009 [2]. All other organochlorines were below limits of detection in all three SPM samples collected in 2009 (Table 16).

Table 16. Concentration of PCBs/OCs associated with suspended particulate matter (SPM) for three samples collected during Sept-Nov 2010 in the River Glomma

	C_{SPM} (µg kg^{-1} dry weight)		
	SPM 1	SPM 2	SPM 3
CB28	<0.5	**0.97**	**3.5**
CB52	<0.5	<0.5	<0.5
CB101	*i*	*i*	*i*
CB118	<0.5	<0.5	<0.5
CB105	<0.5	<0.5	<0.5
CB153	<0.5	<0.5	**0.75**
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
PeCB	<0.3	<0.3	<0.3
α-HCH	<0.5	<0.5	<0.5
HCB	<0.3	<0.3	<0.3
γ-HCH	<0.5	<0.5	<0.5
p,p'-DDE	<0.5	<0.5	<0.5
p,p'-DDD	<1	<1	<1
i: interferences on the GC/ECD chromatogram			

Table 17 presents SPM-associated concentrations of brominated flame retardants (PBDEs) in the three SPM samples. Two BDEs, BDE47 and BDE209 were consistently detected in all three SPM samples. Concentrations were close to 0.1 and 2.3 ng g^{-1} dry weight of SPM for BDE47 and BDE209, respectively. Concentrations of BDE47 were of the same order of magnitude for SPM samples collected in 2009 [2]. Improvements in the limits of detection for BDE209 allowed the consistent measurement in SPM samples in the present study.

Table 17. Concentration of PBDEs associated with suspended particulate matter (SPM) for three samples collected during Sept-Nov 2010 in the River Glomma

	C_{SPM} (µg kg^{-1} dry weight)		
	Sample 1	Sample 2	Sample 3
BDE28	<0.1	<0.1	<0.1
BDE47	**0.13**	**0.06**	**0.10**
BDE49	<0.3	<0.3	<0.3
BDE66	<0.3	<0.3	<0.3
BDE71	<0.3	<0.3	<0.3
BDE77	<0.3	<0.3	<0.3
BDE85	<0.3	<0.3	<0.3
BDE99	<0.2	<0.2	<0.2
BDE100	<0.1	<0.1	<0.1
BDE138	<0.3	<0.3	<0.3
BDE153	<0.3	<0.3	<0.3
BDE154	<0.3	<0.3	<0.3
BDE183	<0.3	<0.3	<0.3
BDE196	<0.3	<0.3	<0.3

BDE205	<0.3		<0.3		<0.3	
BDE209	**2.7**		**2.0**		**2.2**	

Finally the table below (Table 18) shows that only the γ-isomer of HBCD was detected in sample SPM 1 and this is very close to limits of detection. The other two isomers were consistently below limits of detection. The γ-isomer of HBCD is often observed to be the main component in sediments and suspended sediments under urban influence [11].

Table 18. Concentration of HBCD associated with suspended particulate matter (SPM) for three samples collected during Sept-Nov 2010 in the River Glomma

	C_{SPM} (μg kg^{-1} dry weight)					
	Sample 1		Sample 2		Sample 3	
α-HBCD	<0.5		<1.5		<1.5	
β-HBCD	<0.4		<0.6		<0.6	
γ-HBCD	**0.54**		<0.5		<0.5	

3.6.2 Contaminant partitioning in the River Glomma

Since many compounds were detected and quantified in the dissolved phase and associated to suspended particulate matter, the calculation of suspended particulate matter-water partition coefficients for PAHs, some PCBs, organochlorines and BDEs in the overlying water phase was possible. These coefficients were normalised to the fraction of organic carbon, f_{oc} in the suspended particulate matter (on average 5 % at the Glomma River) to obtain K_{poc} for example:

$$K_{POC} = \frac{C_{SPM}}{C_w \cdot f_{oc}}$$

where K_{POC} is the particulate organic carbon-normalised SPM-water partition coefficient for the compound of interest and C_{SPM} and C_w the analyte concentrations associated with SPM and that dissolved in water. Figure 7 shows the logK_{POC} for PAH plotted as a function of compound's hydrophobicity (logK_{ow}). Partitioning of PAHs between water and suspended particulate matter appear to be similar for Exposures 1 and 2 but partition coefficients appear generally higher for Exposure 3. This is the result of the higher SPM-associated PAH concentrations measured in sample SPM 3. The comparison with data from the study conducted in 2009 supports partition coefficients obtained for Exposures 1 and 2.

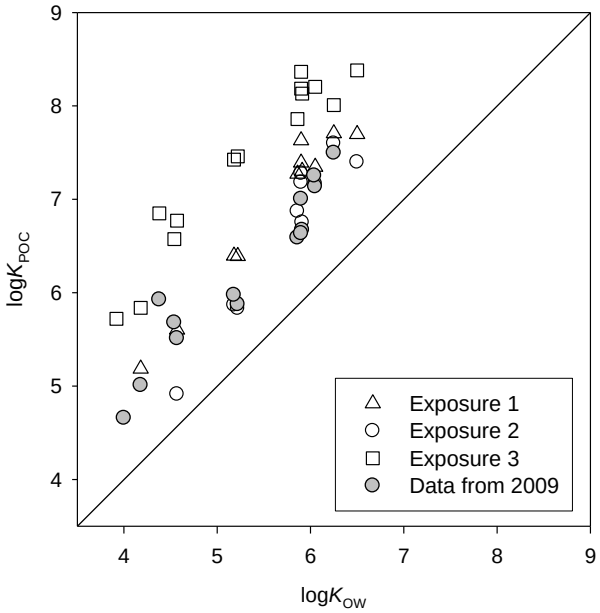

Figure 7. Estimates of particulate organic carbon-normalised suspended particulate matter-water partition coefficients (logK_{POC}) for PAHs for exposure periods 1, 2 and 3 (2010) and comparison with data obtained in 2009

Similar estimations were undertaken for PCBs, OCs and PBDEs and result are given in Table 19. Partition coefficients for CB153 are in line with those from 2009 while in 2010, it was not possible to calculate logK_{POC} for PeCB, HCB and *p,p'*-DEE as these compounds were not detected in the particulate phase. LogK_{POC} for BDE47 was slightly lower than that measured in 2009, while this is the first time it is possible to calculate such a value for BDE209.

Table 19. Estimates of particulate organic carbon-normalised suspended particulate matter-water partition coefficients (logK_{POC}) for PCBs, OCs and PBDEs for exposure periods 1, 2 and 3 (2010) and comparison with data obtained in 2009

Analyte	logK_{ow}	logK_{POC} (L kg^{-1})			
		2009	2010		
			Exposure 1	Exposure 2	Exposure 3
CB153	6.92	7.16			6.79
PeCB	5.18	6.58			
HCB	5.50	4.92			
p,p'-DDE	6.02	6.64			
BDE47	6.60	7.00	6.56	6.26	6.29
BDE209	10.3		7.68	8.09	7.77

4. Recommendations

The measurement of fluxes and input from rivers (to the sea) of trace organic and metal contaminants is one of the objectives of the RID monitoring programme. Main challenges here are the ability to detect and quantify trace organic contaminants at very low concentrations and to obtain reliable measures of average concentrations.

In order to establish a set of recommendations regarding the use of tools tested in RiverPOP projects [1, 2, 6], it is important to reiterate some of their advantages and drawbacks. A comprehensive list of pros and cons based on the actual operation of the sampling techniques and those related to the usefulness of the data collected and the quality of the information was provided previously [1]. Most techniques provide operationally-defined measurements of parameters and this needs to be taken into account when selecting a monitoring method. While it is impossible to measure the true average contaminant concentrations in a river, the aim of monitoring and sampling regime is to obtain an estimate with limited bias and relatively good precision. The objective here is to implement monitoring techniques based on the measurement of specific fractions (dissolved/total) of contaminants in water to improve these estimates. Based on the current RID monitoring programme setup and the data and information obtained during the RiverPOP work, we believe that passive sampling devices and suspended particulate matter sampling with continuous flow centrifugation provided the most attractive possibilities for implementation with the RID monitoring programme. Other techniques such as time-integrative SPM samplers or high volume water sampling have been shown to provide relevant information, however we feel their implementation within the RID programme framework may be more challenging than for the other techniques.

Recommendations provided below relate to operational use, user-friendliness, and data quality and data robustness. Some of these will be relatively general while others are specifically focussed on their application to the RID monitoring programme. We cannot recommend or specify details of sampling programmes with these tools since these should follow general guidelines regarding the design of monitoring plans.

Diffusion Gradient in Thin film devices (DGTs) can be used for period of two to four weeks for the time-integrative measurement of labile metals in water. Ideally, measurements should be accompanied by monitoring of main water parameters that can allow speciation modelling.

While most of these measurements are of a specific fraction of contaminants in water, the estimation of fluxes will require estimates of "whole water" concentrations data. Modelling of speciation for metals or partitioning for nonpolar compounds may be used to infer these "whole water" concentrations. However, supporting data/information and water body-specific knowledge of partitioning may be required for such modelling. While such a procedure may result in some uncertainty, this has to be balanced against other uncertainties such as those arising from the measurement of water flow used in the calculation of fluxes.

4.1 Passive sampling for nonpolar organic substances (with LDPE membranes, silicone strips or SPMDs)

We recommend the use of these tools to improve estimates of time-averaged concentrations of trace hydrophobic contaminants in Norwegian rivers. These tools are particularly useful when concentrations are very low or close to background levels. Passive sampling devices were shown in the present studies to enable substantial improvements in the limits of detection compared with those commonly achieved through bottle sampling. When compounds were below limits of detection in the

present work, these were in the low pg L^{-1} level. These limits of detection are substantially lower than those achieved with standard bottle sampling (in the low ng L^{-1}). The low observed variability in the accumulation of PAHs, PCBs/OCs and PBDEs also supports the use of these tools for long-term monitoring. We therefore recommend the use of these tools to improve estimates of trace hydrophobic contaminant concentrations in Norwegian rivers. This is particularly useful when concentrations are very low. The use of custom-made passive samplers may enable further improvements in limits of detection.

Passive sampling with any type of samplers measures only the dissolved concentration of contaminants. While this is fine for moderately nonpolar compounds, very hydrophobic compounds will also be substantially associated with suspended particulate matter and dissolved organic matter and these fractions may need to be considered when estimating "whole water" concentrations. Modelling and predictions of these fractions may be possible to help estimating total concentrations in the case each fraction cannot be measured separately. More detailed recommendations are provided below:

- Traceability from study design to reporting of the data is compulsory for passive sampling since these measurements rely on highly specific competence throughout the process. This implies that competent personnel with some understanding of passive sampling measurements are needed throughout the process from sampling to data reporting (training maybe needed).
- Application and use of the BSI's Publicly Available Specification providing guidance for passive sampling of surface waters. An ISO standard on passive sampling in surface waters was published in 2011 and these should provide guidelines for designing and conducting a passive sampling study. Passive sampling is mentioned in the chemical monitoring activity guidance document for surface waters established for the EU Water Framework Directive.
- As for many ISO standards, working according to these guidelines does not necessarily mean the data obtained is fit-for-purpose.
- Many quality assurance and control procedures and basics are given in the two standards; however, it is important to mention the use of control samplers and trip control samplers to assess possible contamination of the samplers from preparation, storage or field deployment procedures. Since we are dealing with extremely low concentrations, replication for samplers exposed in water and for control samplers is crucial.
- The monitoring frequency needs to be adjusted to environmental conditions and to the temporal variability of the compounds being measured.
- For relatively variable river systems where the input of contaminants may change with time and processes (snowmelt etc…), we do not expect equilibrium sampling devices to be the most effective passive sampling technique to be used. These can only be used when the temporal variability in concentration is lower than the time needed to reach equilibrium.
- Integrative samplers such as those tested here are able to integrate better these changes in contaminant concentrations. However, the use of performance reference compounds (PRCs) is required to estimate sampling rates in situ. In this respect, the use of multiple control samplers is also relevant to the use of performance reference compounds.
- Almost continuous yearly measurements can be undertaken if monthly exposures are started when others are complete. Longer exposures are possible as long as adequate PRC data can be obtained.
- The selection of a type and conformation (e.g. size, types of PRCs…) of passive sampling device also requires care. This will depend on the compounds of interest (issues with control/blanks) and availability of adequate data and information (e.g. sampler-water partition coefficients) for a reliable calculation of sampling rates and dissolved concentrations. For

example when high sampling rates are needed and an "open cage" is used, SPMDs have been shown not to be robust enough for harsh river conditions.

- High sampling rates are needed for an accurate measurement of brominated flame retardants since concentrations in the dissolved phase are very low.
- When investigating intra-annual temporal variations in concentrations measured by passive sampling devices, it may be important to assess the effect of variation in sampler-water partition coefficients with temperature.

4.2 Passive sampling for trace metals

The behaviour and fate of trace metals is highly dependent on their partitioning among different phases and dissolved metal speciation. The latter comprise the most mobile metal fraction and the most bioavailable species. Sophisticated models have been developed to predict partitioning and chemical speciation of metals. Such models are based on assumptions regarding the state of equilibrium in the system and require important parameters of the water chemistry, including metal concentrations, as input. These geochemical models have formed the basis for further models aiming to predict bioavailability and toxicity of metals toward organisms. Important information regarding trace metals can therefore be gained if the analytical programme includes the parameters necessary for using these models. The WFD guidance document on water chemical monitoring for example states that modelling can be used as additional evidence that environmental quality standards will not be violated, but emphasises the need for careful documentation of model performance. This could be done by comparing model predictions with *in situ* speciation measurements.

Another aspect of relevance to monitoring is the great spatial and temporal variation of trace metal concentrations that can occur in individual rivers. An important question is how well the temporal variation is covered by conventional low-frequency bottle sampling that only captures the momentary situation. Monitoring programs such as RID could therefore benefit from supplementing conventional bottle sampling with a technique that can provide time-weighted average concentrations as well as *in situ* speciation measurements. Many of the recommendation made in the section above are applicable here.

The technique of diffusive gradients in thin films (DGT) can do both; it can be used to measure a time-averaged concentration of the labile fraction (i.e. dissolved inorganic forms and part of the metal bound by organic matter) of metals such as cadmium, copper, zinc, lead, nickel and many more. In combination with conventional sampling and modelling, DGT will provide information that is highly relevant for predicting the bioavailability, mobility and total transport of metals in the river. Below is a summary of advantages and disadvantages with the use of DGT for monitoring purposes. More detailed recommendations are provided below:

- DGT can offer low limits of detection that enable reliable measurements even at background concentrations. This is important for some rivers in Norway.
- Deployment of samplers can be done by non-experts, although training of the field personnel is important. Minimal manipulation of equipment and of the sample in the field is likely to reduce contamination and variability.
- Since membrane fouling is likely to reduce accuracy, deployment should be kept to a duration of days to 2 weeks. However this depends also on the potential for biofouling and the concentrations in water and limits of detection required.
- While DGT can not be used to measure total concentrations, e.g. metal bound by particles is not collected, these data can be used in combination with modelling procedures to predict the speciation of metals in water.

4.3 Suspended particulate matter sampling (centrifugation and SPM traps)

Ideally, passive samplers for hydrophobic compounds should be used together with a technique enabling the measurement of contaminants associated with suspended particulate matter. As long as a secure site with electrical power can be found in the vicinity of the sampling location, use of continuous-flow centrifugation is advised. It has been found to be the simplest and most performant approach to the collection of SPM samples. Work conducted during RiverPOP projects aimed at evaluating the applicability of using a number of techniques for the collection of SPM samples. Based on our experience however, the use of time-integrative SPM samplers or high volume water sampling may be complex and challenging to implement within the RID monitoring framework for example. The time-integrative SPM samplers (SPM traps) require careful deployment and working with large volumes of water to filter or centrifuge to recover particles. The method itself and the fraction of SPM sampled are difficult to define. The use of the high volume water sampler (as tested in 2008) on a routine basis would be impractical and the calibration and assessment of recoveries during the sampling process are difficult to assess. Only small volumes of SPM can be sampled this way. Continuous-flow centrifugation enabled reliable collection of substantial amounts of SPM, adequate for a number of analyses for nonpolar organic contaminants. Some recommendations are provided below:

- Levels of SPM in the river and efficiency of the centrifuge are factors that need consideration when selecting sampling times.
- Based on temporal variations in levels of SPM in water, it may be possible to optimise the deployment of the centrifuge and collect samples representative of when the amount of particles in water is highest.
- A secure site with a source of electrical power for setting up the continuous flow centrifuge is required. This site must be relatively free of contaminants and when the equipment is left unattended, knowledge of the use of the site by others is needed.
- Characterisation of the particle size distribution of SPM samples may be useful to determine whether samples collected are representative of that present in water. If some bias exists in the collection of larger particles, this should be documented.
- Modelling of "whole water" concentration may also be undertaken based on SPM-associated concentrations for the hydrophobic/very hydrophobic compounds.

5. 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 at very low concentrations and to obtain reliable measures of average concentrations. Passive samplers and continuous-flow centrifugation aiming to measure concentrations of contaminants in the dissolved phase and associated with suspended particulate matter, respectively were tested during a field evaluation in the River Glomma in 2010.

Two types of passive sampling devices were used to measure freely dissolved contaminant concentrations. Silicone strips were used for the measurement of PAHs and HBCD while LDPE membranes were deployed for the measurement of PAHs, PCBs/OCs and PBDEs. These were exposed during three consecutive periods of 28 days in the river. A similar cage to that tested in 2009

was used here. This allowed significantly improved limits of detection for PAHs, PCBs and PBDEs as a result of higher sampling rates. These were in the low pg L^{-1} range or below and consistent data was obtained for PBDEs and in particular for BDE209 during the first exposure period. The reproducibility of the measurements was within the expected range.

Suspended particulate matter was sampled on three occasions by continuous-flow centrifugation to measure contaminant concentrations. This, in turn, allowed the estimation of suspended particulate matter-water partition coefficients for some of the contaminants of interest and these were in agreement with those measured in 2009.

Overall, these data combined with those obtained in the Glomma in 2009 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. Recommendations for implementation of some of these tools are provided.

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