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

RIVERPOP

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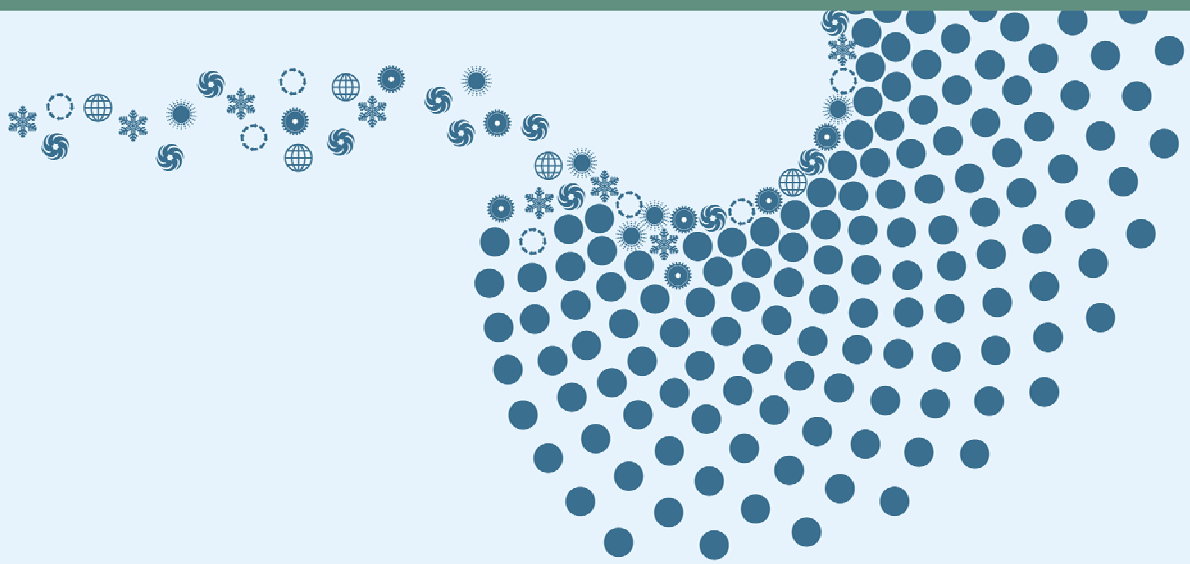

Norsk institutt for vannforskning

Foreword

This report presents results of a study commanded by SFT that aimed to develop and test a number of relatively novel methodologies for the measurement of trace levels of persistent organic pollutants and metals in surface waters. Laboratory and fieldwork in the Drammenselva River (Mjøndalen Bru) was undertaken by NIVA researchers in 2008. It is hoped that, in the future, some of these techniques will become widely used across Norway as part of the Riverine Inputs and Direct Discharges monitoring programme (RID) to estimate riverine fluxes of contaminants. Many members of staff at NIVA contributed to the success of this work. They are Eirik Fjeld, Øyvind Garmo, Katherine Langford, Alfhild Kringstad and Erling Bratsberg.

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Summary

The measurement of riverine fluxes of contaminants is an important task as part of a number of monitoring programmes. The quality, in terms of accuracy and precision, of average contaminant concentrations is therefore very important for adequate estimation of fluxes.
This study was conducted with the aim of developing sampling and analytical methodologies to improve the measurement of contaminant concentrations in water used for further estimation of contaminant fluxes in rivers. These techniques are based on the monitoring of (operationally-defined) specific fraction of contaminants in water. These include fractions associated with suspended particulate matter, dissolved in water or labile to specific tools. In addition, some of these techniques provide information and data for one specific moment in time (at the time of sampling) while others allow time-integrated information on concentration level to be obtained. In general these techniques are able to provide improved limits of detection compared with those commonly achieved with bottle sampling. These aspects are particularly important for the RID monitoring programme. It is hoped that this work lays the foundation for the future use of some of these techniques to improve estimates of the contribution of contaminant fluxes from rivers in Norway to the contaminant burden in the sea.
Objectives of this study were therefore to evaluate the performance of several methods for the sampling of hydrophobic organic contaminants and metals in the Drammenselva River. These included the sampling of particulate-associated contaminants *via* continuous flow centrifugation, time-integrated suspended particulate matter sampling and filtration during large volume water sampling. Analysis included the measurement of PCBs, PBDEs, organochlorines and PFCs. Sampling of dissolved phase contaminants was undertaken using three types of passive sampling devices, namely semipermeable membrane devices (SPMDs), low density polyethylene membranes and silicone strips produced in house, and with large volume water sampling. Compounds of interest were PAH, PBDE, PCBs, organochlorines and organotins. DGT samplers were deployed to measure the labile fraction of trace metals and results were compared with WHAM speciation modelling in an attempt to understand and predict the fraction of metals sampled by DGT. SCF fractionation was also undertaken. Screening of extracts from passive samplers for pharmaceuticals was conducted and semi-quantitative work was undertaken using extracts from passive sampling to measure hexabromocyclododecane. Additional proof-of-concept work was conducted by exposing LDPE and silicone samplers in the Alna River for the monitoring of PBDEs and of different types of DGTs in the Akerselva River.
Overall conclusions of this work are:

- Most techniques based on the collection of suspended particulate matter offer limits of detection in the low pg L^{-1} concentration range.
- Techniques based on the monitoring of dissolved or filtered contaminant concentrations were also in the pg L^{-1} range with passive samplers offering the advantage of integrative sampling for up to periods of 50 days or more.
- Passive sampling with low density polyethylene membranes or silicone strips offer equivalent information to that obtained with semipermeable membrane devices for the monitoring of PAH and PBDEs. In house production of these samplers offer advantages such as control and improvements of blank samplers, use of appropriate or specific performance reference compounds (PRCs). Variability of PAH concentrations measured by the three types of samplers was a factor of 2 to 3. This variability is likely to be associated with the mode of estimation of uptake rates fro PRC data and variability in sampler-water partition coefficients (K_{SW})

- Comparable data was obtained with most of the methods tested here, and when possible logarithms of particulate organic carbon-water partition coefficients (log K_{OC}) were found to be similar to those found in the literature.
- Variability in the data (when concentrations were above limits of detection) was likely due to (i) concentrations close to limits of detection when analytical variability is highest, (ii) variability in contaminant concentrations in water during the field test, and (iii) differences in results from techniques based on discrete and those using continuous/integrative sampling strategies.
- Monitoring of trace metals with DGT and SCF was mostly in agreement with speciation modelling undertaken to understand partitioning of trace metals between different fractions in water.
- Improvements in the operation of some of these techniques are needed while others may be optimised to ameliorate limits of detection and quality of blanks and controls. Possibilities are proposed.

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. For these techniques to be used as part of monitoring strategies such as for the RID programme, costs and operational practicalities for their implementation in different rivers across Norway will be two critical factors.

Utvidet sammendrag

Prosjektets formål

På oppdrag fra SFT har NIVA planlagt og gjennomført forsknings- og utviklingsprosjektet RiverPOP. Prosjektets formål var å utvikle og teste nye metoder for å bestemme konsentrasjoner av persistente organiske miljøgifter (POP) og tungmetaller i elver. Metodene skal være tilpasset miljøforvaltningens behov for beregning av transporten av disse miljøgiftene innenfor RID-programmet (Elvetilførselsprogrammet). Dette programmet måler tilførsler av næringssalter og utvalgte miljøgifter til norske havområder som omfattes av Oslo-Pariskonvensjonen (OSPAR).

Metodene som til nå har vært benyttet for å kvantifisere tilførslene har vært utilstrekkelige for mange miljøgifter. Det har særlig vært et problem med for høye deteksjonsgrenser i forhold til de lave forekomstene i miljøet, samt med prøvenes representativitet (øyeblikksprøver). I dette prosjektet er det har blitt gjort en grundig evaluering av flere teknikker for å bestemme konsentrasjonene av spormengder av organiske miljøgifter og tungmetaller i vann, og prosjektet har lagt vekt på å utvikle enkle og robuste metoder for oppkonsentrering av miljøgifter og tidsintegrert prøvetakning (passive prøvetakere). I stedet for å fokusere på analyser av totale konsentrasjoner i vann, har mange av teknikkene vært basert på å overvåke spesifikke fraksjoner av miljøgifter i elvevann, så som oppløst fraksjon eller fraksjonen bundet til partikulært materiale.

Metoder

Konkret har det blitt utprøvd følgende prøvetakere eller teknikker:

1. Passiv prøvetaker for suspendert partikulært materiale (SPM)
2. Prøvetakning av SPM ved kontinuerlig-støm (continous-flow) sentrifugering.
3. Passive prøvetakere for løst fraksjon av hydrofobe persistente organiske miljøgifter, basert på membraner av LDPE (low density polyethylene) og silikon (silicone strips).
4. For bestemmelse av fri fraksjon av metaller i vann har det blitt testet passive prøvetakere av typen DGT-er (Diffusive Gradients in Thin Films)
5. Metallspesiering har blitt studert ved hjelp av SCF-teknikker (Size Charge Fractionation).
6. Passiv prøvetaker for polare, organiske forbindelser ss. farmasøytiske produkter: POCIS (polar organic chemical integrative sampler).

Prosjektet har i hovedsak vært gjennomført i Drammenselva ved Mjøndalen, men supplerende undersøkelser/metodeutvikling for kvikksølv har vært utført i Alna og Akerselva.

Hovedkonklusjoner

- De fleste teknikkene basert på oppkonsentrering av suspendert partikulært materiale kan tilby deteksjonsgrenser i den nedre del av pg L^{-1} området.

- Teknikker basert på overvikning av den oppløste fraksjonen av miljøgifter, eller filtratet, kan også gi konsentrasjoner i den nedre del av pg L^{-1} området. Dette kan oppnåes ved bruk av passive prøvetakere med en tidsintegrert prøvetakning over en periode på 50 døgn eller mer.

- For overvåkning av PAH (polysykliske aromatiske hydrokarboner – tjærestoffer) og PBDE-er (polybromerte difenyletere – en gruppe bromerte flammehemmere) var passiv prøvetakning med membraner av LDPE (low density polyethylene) eller silikon (silicone strips) like velegnet som de mer tradisjonelle SPMD-er (semipermeble membran devices). Intern produksjon av disse nye prøvetakerene gjør at de har flere fordeler sammenliknet med SPMD-er. Viktige forhold her er kontroll og forbedringer av blindprøver, samt bruk av mer formålstjenlige eller spesifikke referanse-substanser for ytelsekontroll (PRC, performance reference substances). PAH-konsentrasjonene bestemt ved de tre typene prøvetakere varierte med en faktor på 2–3. Dette varierer med metoden benyttet for ekstrapolering av opptaksrater basert på PRC-data, samt variasjonen i partisjonskoeffisientene for prøvetaker-vann (K_{SW}, sample-water partition coefficients).

- De fleste metodene som ble testet, viste sammenliknbare resultater. De beregnede log karbon-vann partisjonskoeffisientene (log K_{CW}) var i overensstemmelse med litteraturdata for de forbindelsene hvor slike data finnes.

- Variasjonen mellom resultatene fra de ulike metodene (for de tilfellene hvor konsentrasjonene var over deteksjonsgrensen) skyltes trolig: (i) høy relativ analytisk variabilitet for nivåer nær deteksjonsgrensen; (ii) variabilitet i de reelle konsentrasjonene av miljøgifter under feltforsøkene; (iii) forskjeller mellom målinger basert på diskrete prøvetakninger (øyeblikkbilder) og kontinuerlige/tidsintegrerte prøvetakninger.

- Resultatene fra overvåkningen av tungmetaller gjort med DGT (Diffusive Gradients in Thin Films) og SCF (Size Charge Fractionation) var i hovedsak i overensstemmelse med modellprediksjoner for metallspesiering av ulike fraksjoner i vann.

- For noen av metodene trengs det en forbedring i de operasjonelle teknikkene, mens andre metoder kan optimaliseres/forbedres med hensyn til deteksjonsgrenser, samt kvaliteten på blindprøver og kontroller.

Konsentrasjoner av persistente organiske miljøgifter (POP) i Drammenselva

For de fleste av de undersøkte organiske miljøgiftene (klororganiske forbindelser, PBDE og PCB) var konsentrasjonene lave og lå nær deteksjonsgrensene i nedre del av eller under pg L^{-1} området. Deteksjonsgrensene som her ble oppnådd var 2–3 ganger lavere enn hva som ellers er oppnåelig ved bruk av tradisjonell prøvetakning med vannflaske. Dette betyr at for en gitt substans hvor deteksjonsgrensen med vannprøveflaske var 1 ng L^{-1} vil en estimert årlig massestrøm i Drammenselva (midlere vannføring ≈ 300 m^3 s^{-1}) kunne være 10 kg $år^{-1}$, mens den med metodene testet her vil ha en deteksjonsgrense på 1 pg L^{-1}.

Tids-integrert prøvetaking av suspendert partikulært materiale (SPM)

En tids-integrerende prøvetaker for suspendert partikulært materiale (SPM) i elver (*in situ*) ble utviklet i prosjektet. Størrelsen av prøvetakeren ble skalert opp fra den originale, slik at den skulle være bedre tilpasset de lave partikkelkonsentrasjoner som kan finnes i norske vassdrag. Testing av prøvetakeren i laboratorium viste at konstruksjonen var vellykket og at prøvene

var representative med hensyn til de tilbakeholdte partikkelfraksjonene. Det ble produsert fire eksemplarer av prøvetakeren, og samtlige ble benyttet i Drammenselva. Det ble her innsamlet prøver av SPM for ekstraksjon og analyse av en rekke miljøgifter (klororganiske forbindelser, PBDE og PCB). På grunn av svært lavt partikkelinnhold i Drammenselva var det ikke mulig å sammenlikne SPM-prøvetakerens representativitet, målt ved TOC (totalt organisk karbon) eller partiklenes størrelsesfordeling, med prøver fra kontinuerlig-strøm (continous-flow) sentrifugering og høy-volums vannprøvetakning. Sammenlikningene måtte derfor kun gjøres med hensyn til konsentrasjonene av POP.

Deteksjonsgrensene for prøvene fra den tids-integrerende SPM-prøvetakeren var i samme område som de fra den kontinuerlig-strøm sentrifugen og fra filtrene i høyvolums-vannprøvetakeren. Deteksjonsgrensene var avhengig av mengden materiale innsamlet, og de var ellers i overensstemmelse med hva som har vært publisert for liknende teknikker. Den analytiske variabiliteten var høyest når konsentrasjonene av de påviste forbindelsene nærmet seg de respektive deteksjonsgrensene. På tross av dette var det et godt samsvar mellom de estimerte konsentrasjonene fra de ulike teknikkene for SPM-prøvetakning.

Det ble funnet muligheter for forbedringer av den SPM-prøvetakeren. Blant annet bør designet endres noe for å minske tendensen til igjengroing (clogging) av inn- og utstrømningsrøret, samt forenkling av prosedyren for tømming av oppsamlet prøvemateriale. Lengre utsettingsperioder vil også øke mengden prøvemateriale og bedre analysenes deteksjonsgrenser.

Passiv prøvetakning av POP

Målet med denne delen av undersøkelsen var å besvare en rekke spørsmål om bruk og forståelse av passive prøvetakere for overvåkning av spormengder av POP-er oppløst i vann. Ved NIVAs laboratorium ble det produsert passive prøvetakere laget av en enkel polymerisk fase, basert på silikon (silicone strips) eller LDPE (low density polyethylene membranes). Preparering av mer enn 20 prøvetakere viste at reproduserbarheten var svært god. Det ble utviklet metoder for å tilsette polymerene referansesubstanser for ytelses-kontroll (PRC: performance reference compounds), samt metoder for påfølgende ekstraksjon og opprenskning av disse. Variabiliteten innen hver type prøvetaker var utmerket, både for de preparerte kontrollene (basert på data av tilsatt PRC) og for de eksponerte prøvetakerene.

Kommersielt tilgjengelige prøvetakere av typen SPMD-er (semipermeable membran devices) ble utplassert i Drammenselva sammen med silikon- og LDPE-prøvetakerene. Eksponeringsperioden var 24 og 51 døgn. For å beregne de tids-veide gjennomsnittlige konsentrasjonene fra massene av POP absorbert i prøvetakeren trengs data på opptaksratene. Disse kan vanligvis bli beregnet med *in situ* kalibrering med PRC. Resultatene var konsistente for samtlige typer prøvetakere, og de var i overensstemmelse med den generelle forståelsen av hvorledes utvekslingen av POP-er skjer mellom vannfase og prøvetaker. PAH-data samlet for eksponeringsperiodene på 24 og 51 døgn var konsistente, og viste at deteksjonsgrensene ble forbedret med lengre eksponering. PAH-konsentrasjonene beregnet var lave, og kun fenantren var over 1 ng L^{-1} (som representerer deteksjonsgrensen for en tilfredsstillende utført prøvetakning med vannflaske).

Tidsintegrert prøvetakning med opptil 50 døgns eksponeringsperiode var mulig for de fleste forbindelsene. PAH-konsentrasjonene bestemt ved de tre typene prøvetakere varierte med en faktor på 2–3. Den var dels avhengig av usikkerheten og variabiliteten i partisjonskoeffisientene for prøvetaker-vann og i eliminasjonsraten av PRC-substansene. Bruken av ulike modeller for å kalkulere konsentrasjonene fra de forskjellige prøvetakerene vil også kunne øke divergensen mellom resultatene fra dem.

For mange av de hydrofobe forbindelsene som ble studert i denne undersøkelsen var den nødvendige prøvetakningsfrekvensen i felt uavhengig av materialevalget i prøvetakeren – så lenge opptakskapasiteten til materialet er tilstrekkelig. Her er polymerenes areal og volum to viktige faktorer som bør vurderes under konfigurasjonen av prøvetakeren.

Det ble ikke funnet noen fordeler med bruk av SPMD-er framfor de to andre prøvetakere basert på membraner av enkelt-polymerer. Data for HBCDD (heksabromsyklododekan) kan tyde på at opptak av store molekyler er bedre i silikonbaserte membraner enn i SPMD-er.

Utsettingene av passive prøvetakere ble supplert med målinger fra en høyvolums vannprøvetaker for å framskaffe data på konsentrasjonene av disse i filtratet. Det ble funnet en utmerket overensstemmelse mellom data fra de passive prøvetakerene og høyvolums vannprøvetakeren. Usikkerheten eller variabiliteten assosiert med metoden for beregning av SDMD-konsentrasjonene – eller forårsaket av oppløst organisk materiale (DOM) og kolloider for høyvolums vannprøvetakeren – vil trolig ikke kunne forårsake forskjeller som er større enn én størrelsesorden.

Informasjon og data i tilgjengelig litteratur synes å støtte bruken av SPMD-er til å overvåke TBT (tributyltinn) i vann. I denne undersøkelsen ble det analysert for en rekke tinnorganiske forbindelser i ekstrakter av SPMD-er. Ingen forbindelser ble detektert, på tross av deteksjonsgrenser i området 20–100 pg L^{-1}.

Det ble utviklet metodologi for bruk av ekstrakt fra passive prøvetakere for analyse av bromerte flammehemmere av typen PBDE. Dette ble gjort på ekstrakter fra SPMD-er, LDPE-membraner og silikon-remser ble undersøkt. Deteksjonsgrensene for PBDE i ekstraktene var 30–500 pg per prøvetaker. Alle PBDE-kongenerene var under deteksjonsgrensene i blindprøvene og kontrollene i LDPE-membranene. Noe PBDE ble påvist i blindprøvene og kontrollene i SPMD-ene. Kontaminering av blindprøver og kontroller ble funnet for silikon-remsene. Generelt kunne bare BDE47 og BDE99 påvises i konsentrasjoner like over deteksjonsgrensene eller signifikant høyere enn i blindprøvene. Konsentrasjonene målt med de forskjellige prøvetakerene var nær 1 pg L^{-1}. Resultatene er lovende og flere alternativer kan bli benyttet for å (i) senke deteksjonsgrensene i laboratoriet, (ii) minske kontamineringen i silikon-prøvetakerene og (iii) øke opptaksratene under eksponeringen.

Det ble forsøksvis gjort beregninger av partisjonering av POP-er når konsentrasjonene i den partikulære fraksjonen og i den oppløste fasen eller filtratet var over deteksjonsgrensene. Log-transformerte partisjonskoeffesienter for partikulært organisk karbon–vann (log K_{OC}) beregnet for noen kongenerer av PBDE og PCB viste at målingene var innen den korrekte størrelsesorden, og sammenlikninger med litteraturdata støtter våre data.

Screening med passive prøvetakereav typen med POCIS (polar compound integrated samplers) etter visse farmasøytiske forbindelser, viste at kun paracetamol og carbamazepine forekom i konsentrasjoner over deteksjonsgrensen i ekstraktet.

Det ble gjort metallanalyser basert på prøver fra DGT-er (Diffusive Gradients in Thin Films) og SCF (Size Charge Fractionation) for å kartlegge konsentrasjonen i ulike fraksjoner i vann. Resultatene kunne i stor grad forklares med metall-spesieringsmodeller. Revers modellering av den totale konsentrasjonen, basert på DGT-data, kan forenkle overvåkningen av spormetaller med tanke på å bestemme massetransporten i elver.

De to typene av DGT-er som ble testet ga liknende resultater. Et papirbasert sorbent-lag er lovende i den videre utviklingen av DGT-teknikken, da dette er lettere å håndtere enn gel-laget.

DGT-prøvetakere for kvikksølv (Hg) med ulike typer diffusjonsgeler og mottaksfaser ble testet. Standard DGT-er ble satt ut i Drammenselva, mens tre ulike typer ble satt ut i Akerselva. Det ble påvist en signifikant kontaminering av kvikksølv (Hg) i blindprøver preparert med henholdsvis et lag agarose gel og et lag spheron-thiol gel. Akkumuleringen av Hg i disse var ikke signifikant. Vanntemperaturen i Akerselva under eksponeringen kan ha hatt en innflytelse på akkumulasjonsratene. Det ble ikke funnet noen signifikant akkumulering av Hg i standard DGT-er i Akerselva. Disse krever imidlertid høye miljøkonsentrasjoner og de er derfor mindre egnet til overvåkning under vanlige miljøforhold. I Drammenselva ble det ikke funnet noe klart mønster i Hg-akkumuleringen i DGT-ene. Før DGT-ene kan benyttes til overvåkning av Hg trengs det forbedringer i blindprøvene. Her finnes det flere muligheter.

Framtidig utvikling

Teknikkene som behandles her er basert på overvåkning av operasjonelt definerte spesifikke fraksjoner av miljøgifter i vann. Disse omfatter fraksjoner assosiert til suspendert partikulært materiale, en løst fraksjon i vann og en labil fraksjon. Noen av metodene gir øyeblikksbilder av konsentrasjonene eller forholdene i vann, mens andre gir tidsintegrert informasjon om konsentrasjonene. Generelt gir de nye metodene muligheter til å forbedre deteksjonsgrensen sammenliknet med tradisjonell prøvetakning med vannflasker. Dette er viktige aspekter for RID-programmet, og prosjektet er ment å danne grunnlaget for en framtidig bruk av noen av disse teknikkene hvor formålet er å bedre estimatene av tilførslene av miljøgifter fra norske elver til havområdene.

Rapporten påpeker mange muligheter for å utvikle de operasjonelle prosedyrene (feltarbeide, prøveinnsamling og -prosessering), deteksjonsgrensene, bruk av data samt kvalitetssikring og pålitelighet knyttet til disse. For den framtidige overvåkningen er det òg viktig å vurdere verdien av informasjonen samlet ved kontinuerlige prøvetakning, så som passive prøvetakere og tidsintegrerte prøvetakere for suspendert partikulært materiale, sammenliknet med informasjon basert på data innsamlet ved et tidspunkt (øyeblikksbilder). I planleggingen av framtidige overvåkningsprogrammer bør disse temaene tas opp, da det er sannsynlig at programmets design og prøvetakningsfrekvens har en like stor – eller større – betydning enn usikkerheten assosiert med de analytiske målingene.

1. Introduction

The presence and release of contaminants into the aquatic environment can result from both natural processes and anthropogenic activity. The presence and levels of these contaminants and mixtures of known and unknown contaminants can pose a direct short- or long-term threat to aquatic organisms and ecosystems in general [1]. Temporal variation in concentration may be dependent on their source (diffuse vs. point) and the physical-chemical characteristics of freshwater systems.
The monitoring of contaminant levels and effects in water and sediments is therefore an integral part of the risk assessment of their presence in the environment. Contaminant monitoring may be undertaken in a number of ways primarily depending on the particular objectives of the monitoring programme and the identity of contaminants of interest. When studies involve the measurement of water quality for example, the estimation of contaminant bioavailability in addition to total concentrations is of particular interest [1, 2]. For water and sediments, this may be measured in terms of concentration in the truly dissolved phase and in pore water, respectively. In addition the rapidly desorbable fraction of contaminants in sediment is a desirable measure of bioaccessibility of contaminants.

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 [3]. 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 RID programme (see below).
While total concentrations are used for the calculation of overall fluxes, an understanding of the speciation of contaminants in water is also relevant to these measurements. Depending on the type of contaminants, their affinity to suspended particulate and dissolved organic matter and colloids, their possible dissociation at different pH, the measurement of the dissolved fraction or that bound to particulate matter, or both, may be important. Particular to many Norwegian river systems, it may be possible that significant amounts of hydrophobic organic contaminant and trace metals may be transported downstream when associated with very fine grained sediments.
The influence of suspended particulate matter may have a significant impact the limits of detection and the reliability of the measurement that may be achieved with bottle sampling for hydrophobic contaminants such as PAHs and PCBs [4, 5]. In addition, standard bottle sampling has been shown to be unable to provide adequate limits of detections for many organic contaminants at environmentally/toxicologically relevant concentrations. In particular, the calculation of contaminant fluxes based on limits of detection may result in a high uncertainty of these estimates. If setting concentrations to half of the LOD, such practise also results in significant uncertainty and there may potentially be orders of magnitude in the difference between actual and estimated fluxes.

The following sections provide (i) a description of the monthly monitoring of Norwegian rivers conducted as part of the riverine input and direct discharges programme (RID), (ii) an introduction to alternative methods for the measurement of contaminants present in the dissolved phase and that associated with suspended particulate matter, and a description of the aims and objectives of the present study.

1.1 RID monitoring programme

The Riverine Inputs and Direct Discharges programme (RID) aims to assess and monitor riverine and direct discharges of contaminants to the Norwegian area of OSPAR's Maritime Area [3]. The area concerned by this monitoring programme can be divided into four coastal areas or sub-regions: the Skagerak, the North Sea, the Norwegian Sea and the Barents Sea. Monthly sampling is carried out in 10 major rivers while quarterly sampling is undertaken in 36 tributaries. The size of the catchments covered by these 46 rivers is representative of approximately 50 % of the Norwegian area draining into relevant waters. Modelling (with Teotil) is undertaken to estimate nutrient loads from unmonitored areas.

Since a total of 247 rivers are presently discharging into coastal waters of Norway, compliance with PARCOM requirements to measure 90 % of the load from Norwegian rivers to coastal areas would be practically and economically difficult. Monitoring was therefore reduced to a viable level with the decision to monitor eight of the major load-bearing rivers. These comprise rivers *Glomma*, *Drammenselva*, *Numedalslågen*, *Skienselva*, *Otra*, *Orreelva*, *Orkla* and *Vefsna*. In addition, two relatively "unpolluted" rivers (*Suldalslågen* and *Alta*) were included for comparison purposes and were monitored with a similar frequency. Since it has been of special importance to estimate the major loads to Skagerak, a proportionally higher number of rivers have been chosen for this part of the country.

A large number of parameters are currently being measured as part of the RID monitoring programme. In 2008 these included:
-pH
-Conductivity
-Suspended particulate matter (SPM)
-Total organic carbon
-Nutrients (total phosphorus, orthophosphates, total nitrogen, ammonium, nitrate/nitrite and silicate)
-Trace metals (As, Cd, Cr, Cu, Hg, Pb and Zn)
-Lindane (γ-HCH)
-PCBs (CB28, CB52, CB101, CB118, CB138, CB153 and CB180)

The reporting of data as part of the RID programme generally includes two values per determinand (i.e. upper and lower estimates). Such estimates are dependent on the limit of detection (LOD) and the number of values below/above limits of detection (Table 1-1). Lower estimates are calculated assuming a value of zero when concentrations are below LOD. Upper estimates are calculated using the LOD as the concentration for values below LOD. Depending on the number of values in yearly datasets that are below LOD, this can result in highly uncertain range of loads and discharges to coastal areas calculated for these particular contaminants.
Guidelines for the selection of methodology for sampling and analysis indicate that for a technique to be deemed suitable for such monitoring exercise, 70 % of samples analysed should be above limits of detection. In 2007, these requirements were not achieved for As, Cd, Hg, Cr, lindane and PCBs. For lindane and PCBs specifically, most if not all data is below LOD. Despite the low limits of detection of methods used for these contaminants, the calculation of total discharges to the North Sea based on limits of detection produces highly unreliable estimates of low precision. For 2007, upper estimates of total discharges of lindane and PCBs into coastal waters of Norway were 13.6 and 82 kg, respectively.

In 2007, water samples from the Glomma and Alna were analysed for the measurement of the concentration of certain pesticides (and their degradation products), pharmaceutical compounds, hormones, antibiotics and industrial chemicals (alkylphenolics and perfluorinated compounds) and results were presented in the 2007 RID programme report [3].

Table 1-1-1. Limits of detection for the various parameters measured in the RID monitoring programme.

	Limits of detection
pH	0.01
Conductivity (mS m^{-1})	0.05
SPM (mg L^{-1})	0.1
TOC (mg L^{-1} C)	0.1
As (µg L^{-1})	0.05
Pb (µg L^{-1})	0.005
Cd (µg L^{-1})	0.005
Cu (µg L^{-1})	0.01
Zn (µg L^{-1})	0.05
Cr (µg L^{-1})	0.1
Ni (µg L^{-1})	0.05
Hg (µg L^{-1})	1.0
γ-HCH (ng L^{-1})	0.2
ΣPCB_7 (ng L^{-1})	0.2 (for individual PCBs)

1.2 Alternative techniques for dissolved-phase contaminant monitoring

1.2.1 Passive sampling for hydrophobic organic compounds

Passive sampling is a technique that may provide certain advantages over more standard laboratory-based whole water sample extraction techniques to monitor contaminants in the aquatic environment [2]. These include the ability to undertake more temporally-representative sampling or by sampling a more relevant fraction of contaminants in water. As shown on Figure 1-1 below, water discharge and amount of suspended particulate matter in the Drammenselva show significant temporal variations. In addition it is possible that even monthly sampling may not be able to detect and integrate all changes in contaminant concentrations that may be associated with these events.

In addition, these tools by accumulating contaminants *in-situ* avoid the need to collect and store water samples, while ensuring minimum contaminant losses, changes in speciation or partitioning during sampling. In short, passive sampling devices can be deployed *in-situ* in water. Since an ISO standard focussing on passive sampling for measuring time-weighted average (TWA) contaminant concentrations in water is currently being developed, it is likely that these techniques will become widely used in regulatory monitoring and risk assessment contexts. In addition, the EU commission has prepared a mandate to CEN to promote the development of adequate standards for WFD ecological/chemical monitoring for which current standard methodology does not fulfil criteria for use in regulatory monitoring and for comparison with EQS. These methods include the sampling/analysis for polycyclic aromatic hydrocarbons, pentabromodiphenyl-ethers, chloroalkanes, organochlorine insecticides, and tributyltin for which passive sampling technology is totally suited.

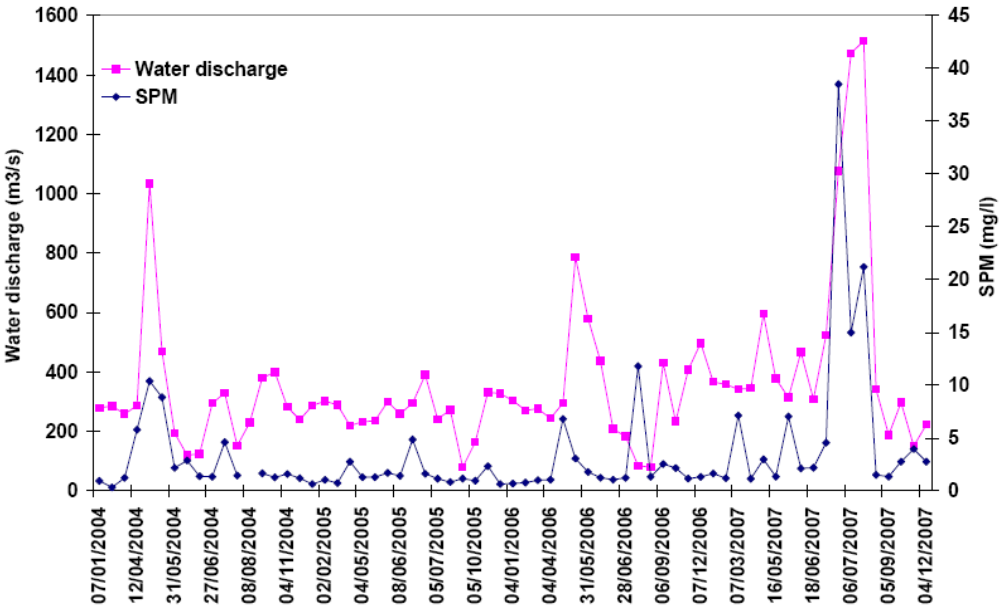

Figure 1-1. Temporal variations in water discharge and SPM level in the Drammenselva river during the period 2004-2008 (graph taken from ref. [3]).

Passive sampling can be defined as a sampling technique for the measurement of the concentration of a compound based on the free flux of analyte molecules from the sampled medium to a receiving phase in a sampling device. This occurs as a result of a difference between the chemical potentials of the analyte in the two media [2]. The net flow of analyte molecules from one medium to the other continues until equilibrium is established in the system, or until the sampling period is stopped.
Analytes are retained in a suitable medium within the passive sampler (the receiving phase, see Figure 1-2). The receiving phase is exposed to the water phase, but without the aim of quantitatively extracting dissolved contaminants. Pollutant adsorption or absorption from water generally follows a first-order kinetic, one compartment model. Amounts of analytes absorbed by passive samplers for nonpolar organics may be represented by a first-order kinetic approach to equilibrium:

$$N = K_{SW}\, V\, C_{TWA} \left[1 - \exp(-k_e t)\right]$$

with N is the amount of analyte absorbed (ng), K_{SW} the sampler-water partition coefficient, V the volume of the sampler (L), k_e the exchange rate constant (h^{-1}), t the exposure time (h) and C_{TWA} is the time weighted average analyte concentration in ng L^{-1}. And where k_e is given by:

$$k_e = \frac{k_O A}{K_{SW} V} = \frac{R_S}{K_{SW} V}$$

where k_O is the overall mass transfer coefficient (see Equation 1), A the surface area of the sampler (cm^2), V the volume of the sampler (cm^3) and R_S the analyte uptake rates (L d^{-1}). In this case, uptake rates (R_S) or equivalent volume of water cleared of analyte by the sampler per unit of time (L h^{-1}) are needed to calculate analyte concentrations in water based on the mass absorbed in the sampler.

Passive sampling measurements in water may be undertaken under kinetic or equilibrium regime, regime controlled by analyte uptake kinetics, sampler characteristics (e.g. material type, sampler surface area and volume of the receiving phase) and analyte characteristics (e.g. the affinity of the analyte for the sampler material). The use of one particular sampler may result for example in sampling under kinetic regime for certain analytes while others may

have reached equilibrium for the same exposure time. Under kinetic regime, the rate of mass transfer of a contaminant from the medium to the receiving phase of the sampler is directly proportional to difference in chemical activity in the water and receiving phase, respectively.

Uptake rates are the result of the mass transfer coefficients in the various compartments that the analyte has to diffuse through during uptake. These compartment include the diffusive water boundary layer (thin film of stagnant water at the surface of the sampler, dependent on sampler conformation and water turbulence), the diffusion-limiting membrane mass transfer is also dependent on the analyte partition coefficients between these phases.

$$\frac{1}{k_O} = \frac{\delta_W}{D_W} + \frac{\delta_M}{K_{MW} D_M} + \frac{\delta_B}{D_B}$$

with δ_W, δ_M and δ_B the boundary, membrane and biofilm layer thicknesses (m), and D_W , D_M and D_B (m^2 s^{-1}) analyte diffusion coefficients in water, membrane and biofilm layers, respectively. Depending on exposure conditions of temperature and water turbulences, mass transfer has generally been shown to be controlled by membrane-side processes for analytes with relatively low log K_{OW} and dominated by transport across the boundary layer for those with high log K_{OW} values [6]. The threshold between these two stages is commonly found for analytes with log K_{OW} between 4.5 and 5.0 [6-8].

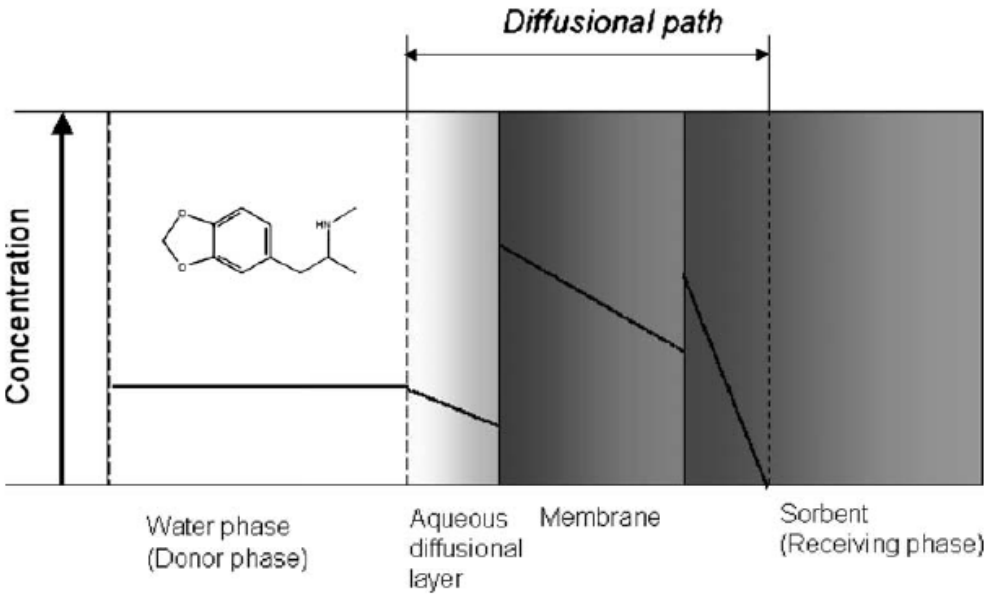

Figure 1-2. Principle of a passive sampling device

These uptakes rates are generally obtained from laboratory-based experiment under known and constant analyte concentrations in water where analyte accumulation in the sampler is observed for a 14-28 day period under various exposure conditions (turbulence and temperature). Since it is difficult to apply uptake rates obtained in the laboratory to field exposure from those a technique based on the use of exposure standards or performance reference compounds can be used to calibrate *in situ* the exchange kinetics of the analyte between the sampler and water [7, 9]. These are labelled (deuterated or ^{13}C-labelled) analogues to the compounds of interest that are spiked into the receiving phase of the sampler. During exposure, their release from the sampler is influenced by the same factors as for the uptake of analytes of interest. It is therefore possible using appropriate models to estimate field-derived uptake rates from PRC release data. This technique is generally applicable to

PAHs, PCBs, pesticides, TBT and other non-polar compounds. PRC dissipation also follows first-order kinetics:

$$N_{PRC} = N_{0,PRC}\left[1 - \exp(-k_e t)\right]$$

where $N_{O,PRC}$ and N_{PRC} are PRC masses in the samplers prior to and following exposure, respectively. Analytes for which the concentration in the sampler approaches equilibrium with the concentration in the water are characterised by significant or even complete dissipation of PRC with similar log K_{OW}. However, negligible or little PRC dissipation is indicative of rates in the linear phase of uptake. The threshold between these two regimes is generally found for PRCs with log K_{OW} of 4.5-5 for exposure periods of several weeks. The use of multiple PRCs spanning a range of log K_{OW} values makes it possible to establish when kinetics of uptake into the sampler are membrane or boundary layer controlled [8].

This technique is, however, not likely to be appropriate for sampling device for polar analyte since analyte binding to the receiving phase of such samplers is not likely to result in isotropic exchange between the sampler and the water phase. A limited number of calibration experiments has been performed so far for polar analytes/sampler systems and little is known of the uptake into the samplers. Deployments of up to 30 days with uptakes rates in the range of 5-10 L day^{-1} for SPMDs or silicone strips have been successful and enabled the calculation Time-Weighted Average (TWA) analyte concentrations in the low pg L^{-1} range. Linear uptake has been observed for compounds with log $K_{OW} > 5.5$ for relatively long exposures.

Many types of samplers for the measurement of nonpolar organic contaminants exist. These include the Chemcatcher [2, 10-12], semipermeable membrane devices [9, 13-16], the membrane-enclosed sorptive coating [17] and more simple single-phase samplers made of simple polymeric membrane such as low density polyethylene or silicone [6, 8, 18-21]. Differences between these samplers can include limits of detection (including range of possible uptake rates), availability of quality sampler-water partition coefficients, validation of the use of PRCs and cost. Recent performance evaluation data for many of these samplers indicate that predicted dissolved phase concentrations generally vary by a factor of 2 while within type of sampler range of concentration amount to approximately 1.3 [8].

1.2.2 Sampling and fractionation of metals

Passive Samplers for metals are based on a similar principle where species diffuse through a diffusion-limiting layer (e.g. hydrogel in the case of the DGT sampling device). Since this is a dynamic system, these samplers do not only measure the free ion fraction but also accumulate the complexed-metal fraction able to dissociate within the time it takes for them to diffuse through the diffusion layer.

The DGT technique permits quantification of an average labile metal fraction representative of the deployment time. It relies on the establishment of a steady concentration gradient through a defined diffusion layer, with one face in contact with the sample solution and the other one in contact with a layer that efficiently binds metal ions [22]. The labile metal fraction comprises species that are able to traverse a hydrogel diffusion layer and release free metal ions during the transport time [22]. After deployment the metal ions are eluted from the sorbent layer and determined with a suitable analytical technique, allowing the calculation of a time-averaged concentration (C_{DGT}) with:

$$C_{DGT} = \frac{m \times \Delta g}{A \times t \times D}$$

where m is the accumulated mass of metal, Δg is the thickness of the diffusion layer, D is the diffusion coefficient of the free metal ion in the diffusion layer and A is the sampling window area. The sorbent layer used in standard DGT devices for analysis of trace metals is made of polyacrylamide hydrogel impregnated with Chelex resin beads [23]. In the present study we also tested a paper-based sorbent layer, containing ester-linked orthophosphoric acid group with high affinity for metal ions [24].

Size charge fractionation (SCF) technique

This method is based on on-site filtration (size fractionation) and ion-exchange (charge fractionation) using a syringe, commercially available filter units, and solid-phase extraction cartridges. Three fractions are determined by direct analysis, namely the total, the filtered, and the filtered & cation-exchanged. Additionally, the fractions retained by the filter and solid phase extraction cartridge can be derived by difference (total minus filtered and filtered minus filtered & ion-exchanged, respectively). Filtration through a filter with pore size 0.45 μm is extensively used, and is the standard operational method for separating particulate from dissolved metal (see e.g. [25, 26] and references therein). Metal fractionation based on passing the water sample through a column packed with cation exchange resin has also been used in several basic studies of metal speciation [27, 28]. For aluminium studies in particular, variants of this technique have been extensively used [29]. Figure 1-3 below shows the various fractions obtained with SCF and DGT, and the properties of species assumed to constitute each fraction. Note that the fraction retained by the cation-exchange cartridge is expected to be similar to the DGT-labile fraction.

Method	Fractions determined		
	Total		
Filtration		Filterable	
Filtration, cation-exchange			Non-exchangeable
Aqueous fraction	Particulate	Dissolved, cationic	Dissolved, anionic
DGT	Excluded	Collected	Mostly excluded

Figure 1-3. Fractionation scheme using DGT and SCF

1.3 Alternative methods for suspended particulate matter-associated contaminant monitoring

A number of possibilities for the measurement of suspended particulate matter-associated contaminants exist [4, 30-39]. These are (i) large volume water sampling, (ii) continuous-flow centrifugation and (iii) the use of time-integrative suspended particulate matter (SPM) samplers (or sediment traps).

Large volume water sampling allows the determination of concentrations both in the particulate phase (retained in the filter) and in the filtered fraction. The fraction collected on the filter is operationally defined since this is dependent on the filter pore size used. When levels of SPM are low, relatively large volumes of water need to be filtered to achieve

reasonable LODs. However, when these are high, this may result in rapid clogging of the filter. Two possibilities are available for quantification of the SPM-associated: Pre-weighed filters can be weighted following sampling and drying to determine the amount of SPM accumulated on the filter (the volume of water extracted is not required). Concentrations can then be expressed in terms of analyte mass per mass of SPM. Alternatively, the filter is quantitatively extracted without weighting and the fraction of SPM-associated contaminants is expressed as mass of analyte per unit of volume of water extracted (in this case the volume of water is absolutely required). Such sampling provide information and data for one point in time and in order to provide representative information to be used in the calculation of yearly fluxes for example, sampling may need sampling programme adjusted with respect to flow for example. Such sampling requires a few hours for the collection of one sample and generally two or three samples per day may be obtained. The filtered fraction may be collected *via* the use of polyurethane foam plugs or adsorptive resin such as XAD resin. The retention efficiency is relatively difficult to control and much uncertainty remains as to the fate of colloid and DOM-associated contaminants. If multiple samples at different depth and across a river are required, such sampling strategy may become laborious. Filters may be pre-burnt for cleaning and sampling is possible for many hydrophobic compounds such as PAHs, PCBs, PBDEs and organochlorine insecticides. Other contaminants such as perfluoroalkyl compounds (PFCs) may also be sampled in such a way.

Continuous flow centrifugation also provides information and data for one point in time [37]. However, sampling may be conducted over several hours or even days. This may be expected to provide slightly more temporally representative data. Pre-cleaned tubing combined with a peristaltic pump is used for collecting water and feeding the water to the centrifuge. Small field scale centrifuges exist however a full lab scale one may also be used when a static and secure monitoring station is available. A field scale centrifuge may generally be run with a power generator. The rate of rotation of the centrifuge drum is partly dependent on the volumetric flow of the feed water. The size of particles that are retained by the centrifuge and resulting grain size distribution of the sample is dependent on the rotation speed. Therefore, such sample collection may present some bias since such a threshold in the SPM collection may give rise in a sediment particle size distribution that may deviate from the original water. The use of a centrifuge with a stainless steel drum and silicone tubing for example may enable the sampling of many hydrophobic organic compounds and PFCs by minimising effect of walls and surfaces and possible contamination of the sample. The processing of up to thousands of litres of water can result in the collection of significant amounts of SPM that may then enable adequate LODs.

Finally, the use of time-integrative SPM samplers may also be possible, although such devices have only recently been used for contaminant monitoring [35, 37, 40]. These devices are based on the fundamental process of sedimentation. Water is directed into the device at a certain velocity (often related to the water velocity outside the sampler) and exits it in a similar way. The velocity decreases significantly within the sampler and allows settling of suspended sediment particles and matter. This allows time-integrated sampling since such device may be left in place for periods of weeks to months. The sampler may then be retrieved and the SPM sample collected for further analysis. Similar issues such as those listed for the centrifugation may be applied to this sampler. The threshold for SPM collection is dependent on the size and configuration of the sampling device. In addition changes in partitioning of contaminant between SPM and water following accumulation into the sampler are unknown.

1.4 Aims and objectives

The aim of this field study was to evaluate and demonstrate the performance of a number of alternative methodologies for the measurement of the concentration of organic and metallic contaminants in river water. These are likely to account for contaminant speciation in water and provide significant improvement in limits of detection compared with common bottle sampling. Improvements in the accuracy and reliability of measurements of concentration of contaminants in water are expected. It is also hoped that these techniques will help reduce the monitoring burden and possibly lower the cost of monitoring while improving the quality and quantity of information collected. Once evaluated and validated, these, in the future, may form a vital part of the RID monitoring programme.

More detailed objectives of this field testing evaluation in the Drammenselva River were to:

- Develop methodologies for the implementation and use of passive sampling for the monitoring of PAHs, PCBs and PBDEs and metals dissolved (or labile) in water of the Drammenselva river
- Evaluate a procedure for the production of silicone strip and low density polyethylene membrane passive sampling devices in house at NIVA
- Compare the performance of commercially available SPMD passive samplers and silicone and LDPE samplers for the measurement of PAHs and PBDEs
- Further our understanding of the fundamentals of passive sampling for hydrophobic organic contaminants (PAHs and PBDEs)
- Provide a comparison of data generated by passive sampling with DGT samplers for metals and data obtained using the SCF methodology
- Provide further DGT and SCF data evaluation with modelling of metal speciation in the Drammenselva
- Develop and test the performance of an integrative suspended particulate matter sampler that would enable the sampling of fine-grained suspended sediment and the measurement of organic contaminants associated with this material (PCBs, PBDEs and PFCs)
- Compare the ability of the time-integrated SPM sampler, the continuous flow centrifuge and large volume water sampling to measure SPM-associated contaminant concentrations (PCBs, PBDEs and PFCs)
- Compare dissolved phase concentrations of hydrophobic compounds measured with passive sampling with those from the filtered fraction following large volume water sampling

Based on the data acquired through this field evaluation, data interpretation is conducted to:

- Provide initial information on the partitioning of hydrophobic substances and metals between the dissolved phase and suspended particulate matter for the Drammenselva river
- Discuss the advantages and challenges associated with the use of these alternative and relatively novel methodologies for the monitoring of contaminants in aquatic systems
- Detail improvements and amelioration that may be undertaken to increase the quality and reliability of the data generated through the use of these methods

2. Methods and procedures

The following chapter presents (i) the RID programme monitoring site for the Drammenselva River where the fieldwork for this project was conducted, (ii) mean values for major water quality parameters for this river obtained from the RID programme monitoring 2008, (iii) techniques used for the measurement of suspended particulate matter-associated contaminants (i.e. integrative suspended sediment sampling, continuous-flow centrifuging and extraction of filters following large-volume water sampling), (iv) techniques used for the measurement of dissolved (or filtered) contaminant concentrations in water (using semipermeable membrane devices, low density polyethylene membrane, silicone strips and large volume water sampling). Finally a summary of the fieldwork undertaken is also provided.

2.1 RID monitoring site description: Drammenselva

The site selected for the present study is the RID programme site on the Drammenselva River. This site is approximately 8 km upstream of the town of Drammen where the river flows into Drammensfjord (see Figures 2-1 and 2-2).

Figure 2-1. RID programme site on the Drammenselva River.

As for all RID monitoring programme sites, the site selected for our study is located in an area of unidirectional flow and where the water is expected to be well mixed. In addition, RID sampling sites are selected as close to the freshwater-seawater limit without seawater influences. Coordinates for the sampling site on the Drammenselva River are Latitude 59.27800 Longitude 11.13400.

Figure 2-2. Map of the Drammenselva showing the RID monitoring site where RiverPOP fieldwork was conducted (red star) situated approximately 8 km upstream of the town of Drammen.

Table 2-1. Mean values for the parameters measured during the RID programme in 2008 and during the RiverPOP fieldwork period (from September to December 2008)

	Yearly mean[a] for 2008	Mean for period Sept.-Dec. 2008[b]
pH	7.04	7.09
Conductivity (mS m^{-1})	3.90	3.69
SPM (mg L^{-1})	4.6	1.04
TOC (mg L^{-1} C)	3.5	3.3
As (µg L^{-1})	0.16	0.1
Pb (µg L^{-1})	0.243	0.065
Cd (µg L^{-1})	0.012	0.008
Cu (µg L^{-1})	1.18	0.83
Zn (µg L^{-1})	4.12	2.49
Cr (µg L^{-1})	0.29	0.23
Ni (µg L^{-1})	0.60	0.36
Hg (µg L^{-1})	<1	<1
γ-HCH (ng L^{-1})	<0.2	<0.2
ΣPCB_7 (ng L^{-1})	<1.4	<1.4
[a]arithmetic mean; [b]Period of 2008 when the fieldwork for this project was conducted		

The temperature of the water during the field test gradually decreased from 10 to 5 °C from September 2008 to November 2008. The level of suspended particulate matter (SPM) was

generally low (~1 mg L^{-1}) and lower than the mean for the year 2008 (Table 2-1). TOC levels indicate that much of the organic carbon in the water is present as dissolved organic carbon rather than particulate. SPM, TOC and DOC were also measured on two occasions during this field test (Table 2-2). Mean values are in good agreement with those from the standard RID programme monitoring.

Table 2-2. Suspended particulate matter (SPM), total organic carbon content (TOC) and dissolved organic carbon content of the Drammenselva river water sampled on the 13/10/08 and 05/11/08.

	Sampling date					
	13/10/08			05/11/08		
	Mean[a]	SD[a]	% RSD	Mean[a]	SD[a]	% RSD
SPM (mg L^{-1})	1.03	0.23	22	1.17	0.29	25
TOC (mg L^{-1})	3.73	0.06	1.6	3.20	0	0
DOC (mg L^{-1})	3.63	0.06	1.6	3.10	0	0
[a]Mean and standard deviation (SD) of triplicate values						

2.2 Monitoring of suspended particulate matter-associated contaminants

Three techniques were employed to estimate the concentration of contaminants associated with suspended particulate matter (SPM) in the Drammmenselva River. Time-integrative sampling was achieved by deploying in situ a device using principles of sedimentation to accumulate SPM over time when exposed in river water. The two other techniques involve the collect of SPM samples at pre-defined times. Continuous-flow centrifugation was undertaken to retain SPM from river water. The final technique involved using a large volume water sampler and the extraction and analysis of the filter.

2.2.1 Time-integrated suspended particulate matter sampler

A simple and relatively inexpensive device was produced following adaptations from the initial design [35]. This time-integrative suspended particulate material sampler is based on the principles of sedimentation. Dimensions of the sampler were increased in order to enable the sampling of a very fine fraction of contaminants present in water (Figure 2-3).

Figure 2-3. Deployment of the suspended sediment sampler in the Drammenselva River. The sampler was attached to a bridge pillar.

Suspended sediment particles are transported in riverine systems as large composite particles or sediment particle aggregates. Such aggregates can be formed of very fine particles. Since the settling velocity of such particles is significantly higher than that of individual finer particles, it is expected that a sampler based on sedimentation processes may be capable of collecting such particles. Since the sampler as designed by Phillips *et al.* [35] was intended for the sampling of small streams, a larger version was produced for this study to enable the sampling of smaller particles transported in relatively larger river systems with low flows.

The integrative nature of the sampling is advantageous since the sampler is capable of integrating natural/anthropogenic variations in levels of SPM and associated contaminants. The result is a composite sediment sample relatively representative of SPM levels during the period of sampling. Depending on the overall level of SPM present in the river water, the exposure duration and the sampling capacity of the sampler, it was expected that the amount of SPM collected would be sufficient for a wide range of analyses for trace contaminant measurements.

2.2.1.1 Sampler design

The design of the sampler is presented in the Figure 2-4. The main body of the sampler is made of aluminium tubing and has an internal diameter of 15 cm (Figure 2-4). Aluminium end-caps fit on each end of the cylinder and 4 mm diameter tubing serves as inlet and outlet for the water to enable river water to travel through the sampler. Inlet and outlet tubes pass through the centre of the end caps and extend through into the main cylinder. An aluminium funnel was positioned at the front of the sampler in order to minimise possible disrupting effects of the sampler on the water flow close to the inlet tube.

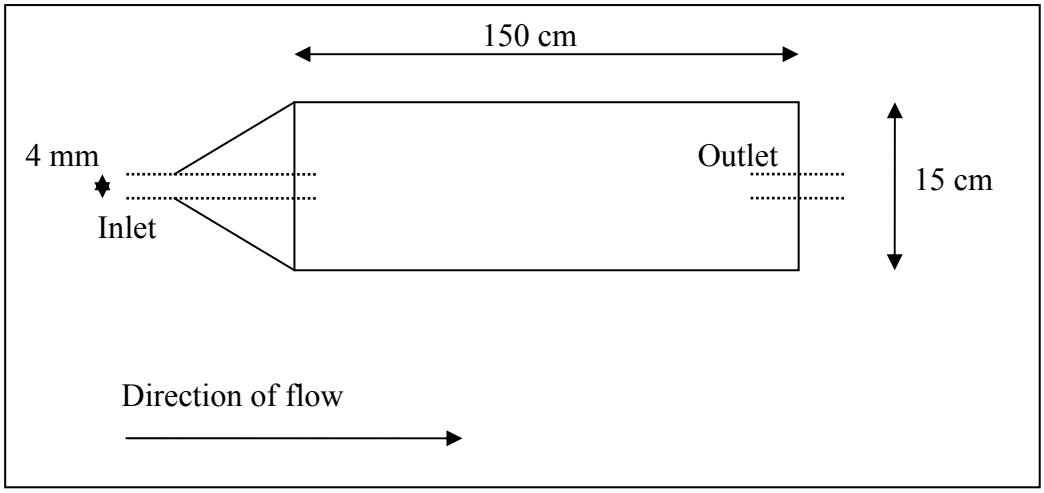

Figure 2-4. Schematic diagram of the suspended sediment sampler adapted from ref. [35] and used during this study.

2.2.1.2 Sampler operation and SPM recovery following exposure

A system was designed to allow the attachment of four time-integrative samplers to a bridge pillar at the RID programme monitoring site. It may also be possible to design a buoy/float and anchor system to position the device in the river.

Inner parts of the sampler were initially cleaned with tap water and that was followed by MilliQ water. Methanol was then used for the final cleaning step. Devices were brought to the field site, filled with Drammenselva river water and fixed to the attachment system. Once

submerged and horizontally installed in the direction of the flow, water enters the inlet and sampling is initiated. The flow velocity in the main tube is significantly reduced when compared with that in the inlet. This leads to sedimentation and accumulation of suspended particulate matter of interest.
Samplers were retrieved following exposure and were plugged with aluminium foil and transported back to the lab. Continuous-flow centrifuging was used to recover particles accumulated in the 50 L of water in the sampler. A low water flow into the centrifuge ensured recovery of most particles accumulated. In addition, it is likely that aggregation of particles during storage of the particles on the sampler facilitates their recovery. Particles were collected from the pre-cleaned stainless steel drum of the centrifuge with a solvent-washed spatula and stored in pre-cleaned glass jars. Jars were stored in the freezer at -20 °C until SPM extraction and analysis.

2.2.1.3 Sampler testing

A wide range of possibilities for testing such devices exist. A number of dedicated tests could be conducted to:

- Evaluate the minimum river flow velocity required to initiate sampling by the sampler
- Evaluate the flow velocity in the inlet as a function of the outer river flow velocity
- Estimate the grain size distribution of the SPM sampled compared with that in the original sample and
- Evaluate the trapping capacity of the sampler.

Here, the evaluation consisted of ensuring that a flow through the sampler was possible during field deployment and verifying that the sampler was able to accumulate suspended particles with an appropriate grain size distribution. Laboratory tests involved passing a suspended sediment solution (20 L) through the sampling device using tubing and a pump. The pumping rate was set to 350 mL min^{-1} (equivalent to a flow velocity of 50 cm s^{-1} approximately in the 4mm diameter inlet tube). Sediment from the Drammenselva were collected and sieved to 1 mm, added to a plastic tank and diluted in water. The water was mixed at a rate that allowed the largest remaining particles to settle. Once this solution pumped through the sampler, the tank was rinsed and filled with tap water that was subsequently flushed through the sampler at a rate of 600 mL min^{-1} for 2 hours. Water samples were collected from the suspended particulate matter solution (S-1), from the sampler outlet when passing the suspended sediment solution through the sampler (S-2, composite sample) and then when tap water was flushed through (S-3, composite sample). At the end of the test, the sampler was opened, the water inside collected and sampled (S-4). Samples were tested for the total amount of suspended particulate matter (mg L^{-1}) and for the particle size distribution in the finest range (<2.2-70 μm).

Figures 2-5 and 2-6 illustrate how the sampler is able to concentrate particles that are passing through since samples S-1 and S-4 shown similar SPM concentrations. Cumulative volumes of particles < 70 μm are also similar and significantly higher than those in the outlet water recovered during flushing of the suspended sediment solution (S-2) or of tap water (S-3). The particle size distribution in the range <2.2-70 μm appears slightly shifted for the sample from inside the sampler (upon termination of the experiment) indicate that the finest particles are not as efficiently retained as slightly larger ones.

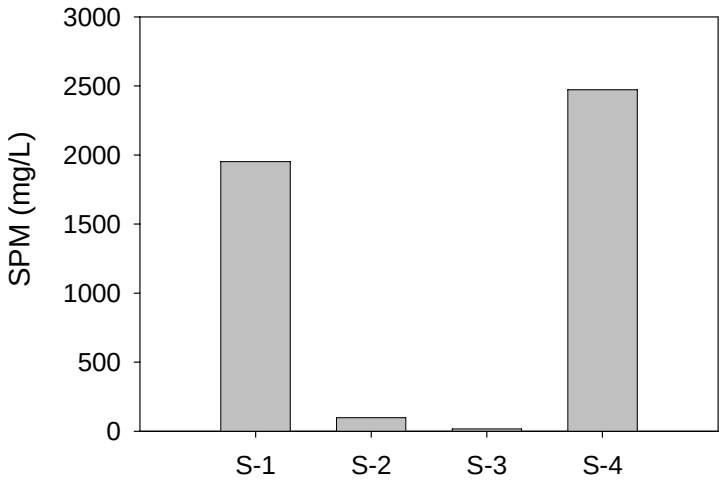

Figure 2-5. Concentrations of SPM in the original suspended particulate matter solution (S-1), in a composite sample of water from the outlet during passage of the solution (S-2), from the outlet when tap water was flushed through (S-3) and from the well-mixed water in side the main cylinder of the sampler (S-4).

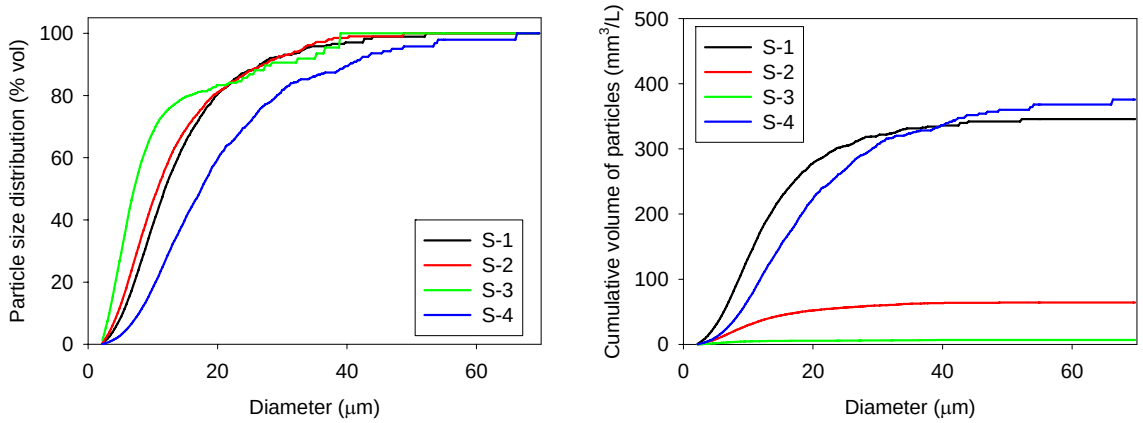

Figure 2-6. SPM grain size distribution and cumulative volumes of particles in the original suspended particulate matter solution (S-1), in a composite sample of water from the outlet during passage of the solution (S-2), from the outlet when tap water was flushed through (S-3) and from the well-mixed water in side the main cylinder of the sampler (S-4).

2.2.2 Continuous-flow centrifugation

The continuous-flow centrifuge was set-up on the river bank of the Drammenselva on a number of occasions and this allowed the sampling of suspended particulate material from the river water. A peristaltic pump was used to deliver river water to the centrifuge using pre-cleaned 1 cm-diameter silicone tubing (Figure 2-7). The pump was adjusted to deliver water at a rate of 1.5 L min^{-1}. Water enters the centrifuge in the rotating collection drum and spins out of the drum while particles are being retained in the drum. Water then exits the centrifuge. The stainless steel drum was cleaned prior to use with three rinses of tap and milliQ water followed by 3 rinses with methanol and hexane. All pre-cleaned equipment was brought to the field site packed in aluminium foil until use.

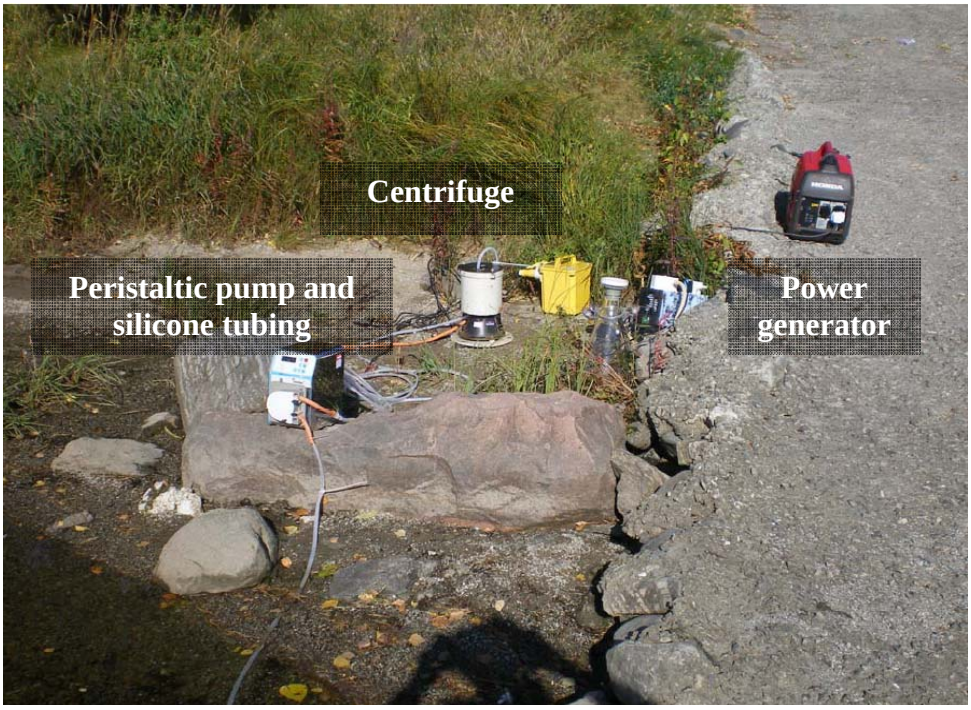

Figure 2-7. Set-up for use of the continuous-flow centrifuge at the RID programme monitoring site on the Drammenselva. The set-up includes the continuous flow centrifuge with stainless steel drum, a peristaltic pump and silicone tubing for delivery of river water to the centrifuge and a power generator for river bank use.

The power generator was placed away from the centrifuge during use. Upon use, the centrifuge drum was brought back to the laboratory and particulate matter was collected from the centrifuge drum with a pre-cleaned stainless steel spatula. When the amount of SPM was very low, milliQ was added to resuspend SPM in the centrifuge and the solution was filtered with a 0.45 μm cellulose nitrate filter. SPM was collected from the filter and stored in pre-cleaned glass jars in the freezer until extraction and analysis. SPM samples were freeze dried prior to extraction.

2.3 Monitoring of trace metals: Passive sampling, SCF and speciation modelling

DGT devices were eluted using standard methods used for these devices at NIVA and extracts were analysed by ICP/MS. SCF extracts were also processed and analysed using standard procedures at NIVA. These may be found in previous reports [41, 42].

Calculation of the chemical speciation of metals in the river was performed using WHAM [43], incorporating Humic Ion-Binding Model VI [44]. Average pH measured during the monitoring period was used as input to the model. Dissolved organic carbon (DOC) was assumed to be the same as the measured total concentration of organic carbon (TOC). The concentration of humic substances was therefore derived from the average TOC measurements: 50% of the measured TOC was assumed to be humic substances, which were themselves assumed to be 50% carbon (Suwannee river fulvic acid is 52% C). Fulvic acid was assumed to constitute 100% of the humic substances. Concentrations of major ions were unfortunately not measured during this campaign. The ionic strength was therefore estimated from the measured conductivity, using an empirical formula taken from [45]. Concentrations of Na, K, Mg, K, Cl, and SO_4 were thereafter calculated based on the assumption that their

relative concentrations corresponded to earlier measurements in Lake Tyrifjorden [46]. The major ions and the average concentrations of Mn Cd, Zn, Ni, Cu, and Pb were assumed to be present exclusively as free ions, inorganic complexes, or bound to fulvic acid. The concentrations of filterable Al and Fe indicated supersaturation with respect to solid $Al(OH)_3$ and $Fe(OH)_3$. The concentrations of truly dissolved Al and Fe were therefore estimated from the corresponding solubility products. Colloids (for example comprised of $Al(OH)_3$ or $Fe(OH)_3$) passing the filter may also be associated with other trace metals, but such species were not considered.

2.3.1 Analysis for trace metals and Hg

The standard NIVA method was used for analysis of Hg in the DGT extracts from the Drammenselva [47]. However, for extracts from the DGTs exposed in the Akerselva, DGTs were extracted in 1 mL of nitric/hydrochloric acid (50:50) that was subsequently diluted to 10 mL for analysis using a Lumex RA-915+ portable multifunctional atomic absorption spectrometer with Zeeman background correction. Liquid samples (extracts of DGTs) were analysed using the cold vapour technique with the RP-91 attachment. Solvent blanks and DGT blanks were used throughout.

2.4 Contaminant monitoring with passive sampling devices

The monitoring of hydrophobic organic contaminants in the dissolved phase was undertaken using 3 types of devices. These were semipermeable membrane devices (SPMDs), low density polyethylene membranes (LDPEs) and silicone strips (Figure 2-8). While SPMDs are commercially available, LDPEs and Silicone strips were prepared in the laboratory. Characteristics of the various samplers can be found in the table below. All samplers were made to have similar surface areas, however the nature of materials used resulted in different sampler volumes. A list of the different performance reference compounds used with the different samplers is also provided (see Table 2-3).

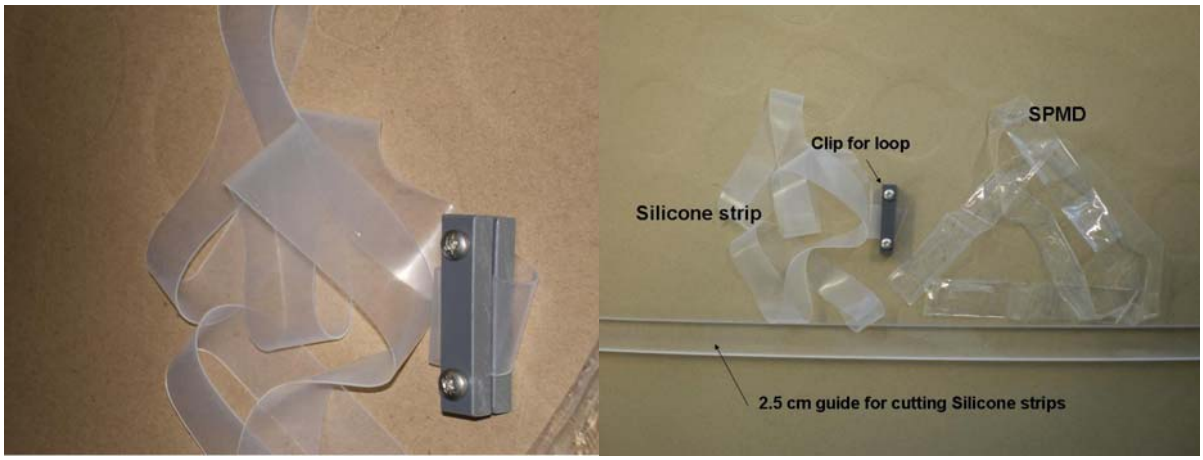

Figure 2-8. Silicone strip with a mounting clip (left) and silicone strip and a semipermeable membrane device (right).

Table 2-3. Configuration and characteristics of the 3 passive sampling devices.

	SPMD	Silicone	LDPE
	LDPE membrane &	AlteSil™ silicone	LDPE membrane

	triolein (1 mL)	polymer	
Length (cm)	92.5 (*nominal*)	92	92
Width (cm)	2.5 (*nominal*)	2.5	2.62 [*2.53-2.71*]
Thickness (μm)	-	567 [*470-620*]	81.3 [*78.9-84.7*]
Surface area (cm2)	460	460	460
Volume (cm3)	4.95 (*nominal*)	13.05	1.95
List of PRCs	d_{10}-PHE d_{10}-ACE d_{12}-CHRY d_{10}-FLUE d_{12}-BeP	d_{10}-PHE d_{10}-FLUE d_{10}-ACE d_{10}-FLUO d_{12}-CHRY	d_{10}-PHE d_{10}-FLUE d_{10}-ACE d_{10}-FLUO d_{12}-CHRY

2.4.1 Semipermeable membrane devices

Semipermeable membrane devices are commercially available sampling devices composed of triolein enclosed into low density polyethylene tubing. Standard size SPMDs (92 cm long, 2.5 cm wide) were purchased from Exposmeter AB (Sweden).

2.4.2 Low density polyethylene membrane preparation

Lay-flat low density polyethylene (LDPE) tubing was purchased from Brentwood Plastics, Inc (US) since this is the tubing used to prepare SPMDs. Membrane-water partition coefficients (K_{SW}) are available for this particular LDPE and it has recently been used in many studies [6, 8, 18]. The tubing was cut along the two edges resulting in 2.5 cm wide LDPE membranes. The length was adjusted to the length of commercially available SPMDs and mounting loops were made using a heat-sealer. Samplers were rinsed first under tap water, then with MilliQ water and then dried with a clean tissue. Samplers were pre-cleaned by soxhlet extraction with methanol and hexane for 8 hours. The extraction was repeated with fresh solvents. This step aims to ensure the quality of blanks and the removal of possible oligomers from the polymer. Samplers were left to dry in a fume hood before spiking with performance reference compounds (PRCs, see Table 2-4). A series of deuterated and fluorinated PAHs dissolved in methanol was used here. The spiking procedure involved bringing in contact each sampler with a 50:50 methanol/water solution fortified with 5 μg of deuterated PAHs and 4 μg of fluoro-PAHs in a pre-cleaned 50 mL glass tube [6]. This solution was then shaken on an orbital shaker at 100 rpm for 72 hours. Samplers were then removed from the solution, rapidly dried with a clean tissue to remove solution from the surface and let to dry for 1 minute before being stored in clean jars at -20 °C until deployment.

Samplers were 92 cm long, 2.6 cm wide and membrane thickness was on average 80 μm.

Table 2-4. Within-batch reproducibility of loading PRCs into LDPE membrane samplers.

	PRC mass spiked (ng) in LDPE membrane samplers		
	Mean[a]	SD[a]	%RSD
d_{10}-ACE	2917	284	10
d_{10}-FLUE	3427	205	6
d_{10}-PHE	4871	303	6
d_{10}-FLUO*	35.1	2.9	8
d_{12}-CHRY	5526	896	16

[a]Mean and SD based on 8 replicates *Peak area/response on GC/MS chromatogram

The within batch reproducibility for spiking performance reference compounds into LDPE membranes is excellent with most relative standard deviations under 10 % (see Table 2-4). This uncertainty accounts for errors and uncertainties associated with sampler production to certain dimensions, sampler to solution volume ratios during spiking, sampler extraction and of the analytical determination of PRCs.

2.4.3 Silicone strip sampler preparation

AlteSil™ silicone sheets were purchase from Altec Ltd (Cornwall, UK) and strips with a width of 2.5 cm were cut. Membrane-sampler partition coefficient data for PAHs and PCBs is available for this polymer. The thickness of the silicone sheet was on average 570 μm and length was adjusted to obtain a similar sampler surface area as SPMDs and LDPE membranes. Samplers were first rinsed under tap and MilliQ water, dried with a clean tissue and soxhlet extracted with mixtures of methanol/hexane/pentane for three days. This aimed to clean the sheets and remove oligomers that can interfere with the chromatography.

A similar procedure to that used for LDPE membranes was used for spiking performance reference compounds into the silicone material. In short, silicone strips were mixed into a 150 mL (50:50 water/methanol) solution fortified with 4 μg (nominal) of a range of deuterated PAHs. This was left on an orbital shaker for 72 hours at 100 rpm. Equilibrium is expected to be reached within 8 hours. Samplers were removed from solution, dried with a clean tissue and left to dry in the fume hood for 1 minute prior to storage in clean jars at -20 °C. Purpose-made clips were soxhlet cleaned prior to use to produce mounting loops with the samplers.

Table 2-5 Within-batch reproducibility of loading PRCs into silicone strip samplers.

	PRC mass spiked (ng) in silicone strips samplers		
	Mean[a]	SD[a]	%RSD
d_{10}-ACE	3744	317	8
d_{10}-FLUE	4926	456	9
d_{10}-PHE	6349	837	13
d_{10}-FLUO*	53.1	4.9	9
d_{12}-CHRY	6025	498	8
[a]Mean and SD based on 8 replicates *Peak area/response on GC/MS chromatogram			

The within batch reproducibility for spiking performance reference compounds into silicone strips is excellent with most relative standard deviations under 10 % (see Table 2-5). Such uncertainty includes errors and uncertainties associated with sampler production to specific dimensions, sampler to solution volume ratios during spiking, sampler extraction and of the analytical determination of PRCs.

2.5 Sample extraction and analysis for organic contaminants

2.5.1 Passive sampler extraction and analysis for PAHs and PBDEs

SPMD: Sampler were cleaned thoroughly by washing with de-ionised water and wiped with a clean tissue. Samplers were placed in a suitable pre-clean glass jar, and 100 ml hexane

(Rathburn HPLC Grade) was added. The container was sealed with aluminium foil and a lid and stored for 24 hours in the dark. After 24 hours, the hexane was replaced with fresh solvent Extracts were spiked with internal standards for PAHs (d_8-naphthalene, d_{10}-biphenyl, Acenaphthylene-d_8, d_{10}-pyrene and d_{12}-perylene) and PBDE (BDE30, BDE181, ^{13}C-BDE209). 100 ml hexane was added to the sample and the sample stored for 24 hours. Hexane extracts were combined after 24 hours. Hexane extracts were reduced under nitrogen until volumes were close to about 0.5 ml. Extracts were quantitatively transferred to a test tube and made up to 2mL with cyclohexane (JT Baker, Ultra Resi-analyzed). Extracts were split into two, for separate clean up for PAH and PBDE fractions. PAH extracts were cleaned with acetonitrile (Scharlau, HPLC Grade) and reduced to 200 µL for analysis by GC/MS. The PBDE fraction was cleaned with H_2SO_4 (Scan Pure 96% sulphuric acid). Extracts in cyclohexane were transferred to a GC vial, and reduced to a final volume of 200 µL for analysis on GC / MS.

LDPE membranes and silicone strips: The same procedure and standard solutions as used for SPMD and described above was used. However, methanol (Rathburne, HPLC grade) was used as extraction solvent instead of hexane.

PAH analysis: Extracts were analysed on a HP-6890 Plus gas chromatograph equipped with a HP 5973 Mass Selective Detector operated in single ion monitoring mode (SIM) with electron impact ionisation (70 eV). The identification was made by comparing retention times and molecular ion 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 (0,25mm i.d. and 0.25µm film) and with a helium 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 the rate of 15 °C min^{-1} (held for 6 min). Injector, transfer line, ion source and quadruple temperatures were set to 300, 280, 230 and 150 °C, respectively.

PBDE analysis: Extracts were analysed on a HP-6890 Plus gas chromatograph equipped with a HP 5973 mass selective detector operated in single ion monitoring mode (SIM) with chemical negative ionisation (NICI) and methane as reagent gas. The identification was made by comparing retention times and characteristic ions (486/488 for BDE-209 and 79/81 for all the others) 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 30 m Rtx-1614 column (0,25mm i.d. and 0,25µm film). The temperature was held for 2 min at 120 °C before ramping to 300 °C at a rate of 6 °C min^{-1}. The final step was an increase to 330°C at the rate of 20 °C min^{-1} (held for 6 min). The flow was kept at 1.2 mL min^{-1} for 13 min then ramped to 1.4 mL min^{-1} at the rate of 0.1 mL min^{-1} (held for 8 min). Injector, transfer line, ion source and quadrupole temperatures were set to 320, 325, 250 and 106 °C, respectively.

2.5.2 SPMD extraction and analysis for PCBs and TBT

Sampler clean up to remove debris and biofouling and dialysis was the same as described above. Internal standards for PCBs (CB30, CB53, CB204) and TBT (tripropyltinn, tripentyltinn) were added to the solvent extract. Once reduced under nitrogen, extracts were split into two fractions for either PCB or TBT analysis. PCB extracts were diluted with dichloromethane (Rathburn, HPLC grade) to 2 mL and cleaned up with gel permeation chromatography (LC / GPC). Purified extract were reduced with nitrogen. Solvent change to

cyclohexane was undertaken and extracts were cleaned with H_2SO_4 and a similar volume of extracts to that obtained for PBDE in the section above was used.

TBT extract were transferred to 100 mL centrifuge tubes, and 25 mL of 0.1 M acetatbuffer (Merck, Sodium-Trihydrat, pro analysi) was added. The pH was adjusted to between 4 and 5 with 4 M HCl (Merck, pro analysi). Sample derivatisation was undertaken with 1 mL of NaEt4B (Alfa Aeasar). Ten mL of hexane were added and spanned. The hexane phase was collected and this step was repeated with fresh hexane. Hexane extracts were combined and reduced under nitrogen to approximately 1 ml. Extracts were transferred to GC vials and further reduced under nitrogen to a final volume of 500 µL for analysis on GC / MS.

PCB analysis: Extracts were analysed on an Agilent 6890 N gas chromatograph equipped with a micro Electron Capture detector (GC/ECD). 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 (0,25mm i.d. and 0.25µm film). 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 at rates of 2 and 20 °C min^{-1}, respectively (held for 6 min). Injector and detector temperatures were set to 255 and 285 °C, respectively.

TBT analysis: Extracts were analysed on an Agilent 6890 N gas chromatograph equipped with a Agilent 5973 Network mass selective detector operated in single ion monitoring mode (SIM) with electron impact ionisation (70 eV). The identification was made by comparing retention times and characteristic ions in standard solutions and sample extracts. The quantification was performed with both internal and external standards. Analytes were separated on a 30 m DB-5 column (0,25mm i.d. and 0.25µm film) and with a helium flow of 1 mL min^{-1}. The temperature was held for 2 min at 50 °C before ramping to 230 °C at a rate of 10 °C min^{-1}. The final step was an increase to 310°C at the rate of 25 °C min^{-1} (held for 2 min). Injector, transfer line, ion source and quadrupole temperatures were set to 280, 280, 230 and 150 °C, respectively.

2.5.3 SPM extraction and analysis for PCBs and PBDEs

Freeze-dried sediments were weighted in 50 ml beaker. Samples were mixed with hydromatrix (Varian), mixed into a homogeneous mixture with steel spatula. The sediment mixture was transferred to the Accelerated solvent extraction cells. Standard internal standard solutions of PCB (CB30, 53 and 204) and PBDE (BDE30, BDE181 and ^{13}C-BDE209) were added to sediments.

Samples were extracted using an ASE 200 with the extraction using a mixture of dichloromethane and cyclohexane (50:50). Samples were extracted three times 5 minutes at 100 °C, and a pressure of 2000 PSI. 60 mL samples were collected. Extracts were reduced to 1 mL and a similar clean up with sulphuric acid as described previously was undertaken. Extracts were reduced to 200 µL for analysis.

2.5.4 SPM extraction and analysis for PFCs

Freeze-dried sediment samples were mixed with acidified MilliQ water (acetic acid) and methanol (5%) and sonicated. Plastic bottles were left for the sediment to settle and the liquid phase was passed through an StrataX SPE cartridge (200 mg) from Phenomenex. The extraction step was repeated and the supernatant was also passed through the cartridge. PFCs

were eluted from the SPE cartridge with methanol. Analysis of perfluorinated compounds was performed by LC/MS/MS. Separation used an Aquity UPLC BEH C_{18} column (1.7 μm, 2.1 mm id, 50 mm) with a flow rate of 0.6 ml/min and a column temperature of 60 ^{o}C. Compounds were separated using a gradient elution programme with water (10 mM ammonium acetate) and methanol (10 mM ammonium acetate). The mass spectrometer was operated in ESI negative mode using multiple reaction monitoring. The cone gas used was nitrogen at a flow rate of 47 l h^{-1} and the desolvation gas flow was 1000 L h^{-1} with a desolvation gas temperature of 400 ^{o}C and a source temperature of 100 ^{o}C. Mass spectrometer conditions were optimised.

2.5.5 Filter and polyurethane foam extraction and analysis for PCBs and PBDEs

Samples of PUF plugs and filters were kept in pre-clean glass jars and stored in the freezer at -20 °C. Samples were quantitatively transferred to soxhlet extraction apparatuses and extracted using hexane and methanol (50:50). Internal standards (for PCBs and PBDEs) were added to filters and PUF plugs prior to setting up soxhlet extraction. The extraction procedure was repeated with fresh solvents and soxhlet extractions were run for 8 hours. Solvent batches were combined and reduced under nitrogen. 2 mL samples were split and one fraction was kept in case more analysis was required. The second fraction was clean-up with H_2SO_4 and reduced to 100 μL and analysis by gas chromatography.

2.5.6 Screening for hexabromocyclododecane

Aliquots (50 μl) of the PBDE/PCB extracts were taken and evaporated to dryness under nitrogen before being reconstituted with acetonitrile in preparation of LC/MS/MS analysis.

Liquid chromatography – mass spectrometry (LC/MS) analysis used a Waters Aquity UPLC coupled to a Waters Quattro Premier XE triple quadruple mass spectrometer. 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 and acetonitrile using a gradient elution programme at a flow rate of 0.6 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 kV, the source temperature 120 ^{o}C and the desolvation temperature 400 ^{o}C. The nitrogen cone gas was at a flow rate of 50 L h^{-1} and the argon desolvation gas at 1000 L h^{-1} with cone and collision voltages of 15 V. Two MRM transitions were used for each isomer 640.5 → 79/80.

2.5.7 POCIS samplers and analysis for pharmaceutical compounds

Polar Organic Chemical Integrative Samplers (POCIS), marketed as AQUASENSE-P in Sweden can be used to monitor hydrophilic contaminants in water (see Figure 2-9). Analytes that have been shown to accumulate in these samplers include pesticides such as triazine and phenyl urea herbicides or pharmaceuticals compounds such as prescription drugs, steroids, and antibiotics [48-54].

2.5.7.1 Sampler preparation

The sampler is composed of two metal rings designed to hold the adsorbent medium between two polyethersulfone (PES) membrane sheets. Samplers prepared “in house” for this project were similar to the “pharmaceutical” version of the sampler and contained 200 mg of OASIS HLB sorbent enclosed between two PES membranes (pore size of 0.1 μm). Since the total surface area of the sampler (including both sampling sides) is approximately 41 cm^2, the surface area to mass of sorbent ratio was close to 200 cm^2 g^{-1}.

All equipment and glassware used in the preparation of the samplers were rinsed with tap water followed by distilled water and methanol. Clean up of the OASIS HLB sorbent was undertaken by soaking in methanol and was dried prior to assembling the samplers. Triplicates samplers were prepared and one trip blank was produced to establish the quality of the sampler production and estimate possible contaminant during sampler production, manipulation in the field and during sampler extraction and analysis.

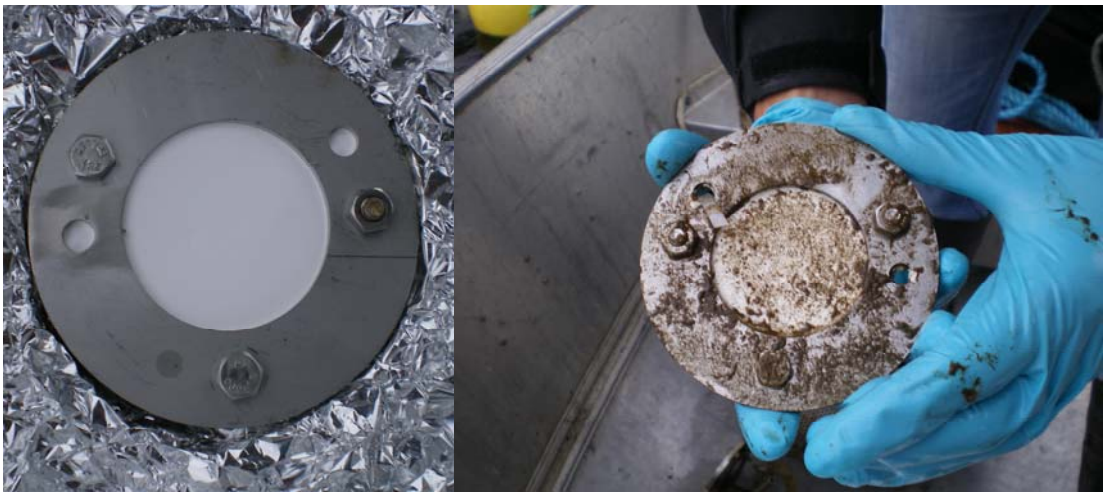

Figure 2-9. POCIS passive sampling devices prior to deployment (left) and following exposure in the Drammenselva River.

2.5.7.2 Sampler extraction and analysis for pharmaceutical compounds

Once returned to the laboratory, samplers were rinsed with distilled water to remove biofouling and were dismantled to collect the sorbent. Pre-cleaned plastic solid-phase extraction columns with a PTFE frit were used to collect the sorbent. Analytes were eluted from the column using methanol with 6 mL methanol, followed by 6 mL methanol (0.1% formic acid) and finally methanol (0.1% ammonium hydroxide). Eluants were combined and evaporated under nitrogen to approximately 1 mL in preparation for analysis by LC/MS/MS [52].

Liquid chromatography – mass spectrometry (LC/MS) analysis used a Waters Aquity UPLC coupled to a Waters Quattro Premier XE triple quadruple mass spectrometer. Analytes were separated on an Aquity BEH C18 1.7 µm column (2.1 x 50 mm) (Waters, Sweden). The mobile phases for optimised separation were modified water (10 mM ammonium acetate) and modified methanol (10 mM ammonium acetate). A flow rate of 0.35 mL min^{-1} was used.

2.6 Drammenselva River fieldwork

The following tables provide a summary of the fieldwork undertaken for this project including when sampling with the various techniques was undertaken.

Table 2-6. Sampling programme for this field evaluation.

Date	Time	Sampling procedure
15/09/08	12:30	Deployment of SPMDs (x5) and silicone strips (x5) samplers (PAHs & PBDEs)
		Deployment of DGT metals (x3) and “P” (x3)

	13:00	Deployment of SPMDs for PCBs/TBT (x3)
		Deployment of POCIS devices for pharmaceutical compounds
		SCF sample collection
29/09/08	12:00	Deployment of SPMDs (x5), silicone strips (x5) and LDPE membranes (x5)
	17:00	Suspended sediment samplers deployed
		Continuous-flow centrifugation sample collection (x1)
13/10/08	12:00	Retrieval of DGTs and deployment of new ones
	12:30	SCF sample collection
		Retrieval of SPMDs for PCBs/TBT and deployment of new ones (x3)
		Retrieval of POCIS devices
		Continuous-flow centrifugation sample collection (x1)
		Sampling for SPM/TOC/DOC measurement (x3)
23/10/08	12:00	Retrieval of SPMDs (x5), silicone strips (x5) and LDPE membranes (x5)
	15:00	Retrieval of suspended sediment samplers
		Continuous-flow centrifugation sample collection (x1)
		Large volume water sampling (x2)
05/11/08	12:45	Retrieval of DGT Metals (x3) and "P" (x3)
	13:00	Retrieval of SPMDs (x5) and silicone strips (x5)
		Retrieval of SPMDs for TBT/PCBs (x5)
		Large volume water sampling (x2)
		Retrieval of SPMDs for TBT/PCBs
		Sampling for SPM/TOC/DOC measurement (x3)

Table 2-7. Review of sampling dates and passive sampler exposure duration

Sampling procedure	**Dates (in 2008)**			**Duration (days)**
SCF sampling	15-Sep	13-Oct		
DGT deployment 1				28
DGT deployment 2				23
POCIS deployment				28
SPMD TBT/PCBs deployment 1				28
SPMD TBT/PCBs deployment 2				23
SPMD/Si 7 week deployment				51
SPMD/Si 3.5week deployment				24
Continuous-flow centrifugation	29-Sep	13-Oct	23-Oct	
Suspended sediment sampling				24
Large volume water sampling	23-Oct	05-Nov		

2.7 Additional work in the Alna and Akerselva Rivers in Oslo

This project was complemented with further evaluation of some of the devices tested in the Drammenselva with deployments in the Alna and Akerselva Rivers in Oslo since generally higher concentrations of PAHs, PBDEs and Hg may be expected in these rivers compared with levels in the Drammenselva River.
LDPE membranes and silicone strips (replicates of each type of samplers) were exposed in the Alna River for one month from December 2008 to January 2009 (Figure 2-10). In a similar period, two specific types of DGT devices supposed to be more adequate than standard devices were tested at three sites in the Akerselva in order to evaluate with differences in labile concentrations of Hg could be observed at these different sites [55, 56].

Figure 2-10. Deployment cage for the LDPE membrane and silicone samplers exposed in the Alna River. Note the wide stainless steel mesh allowing increased water turbulences around the samplers. This is likely to contribute to increasing uptake rates and lowering LODs.

3. Results

This section presents data on the monitoring of contaminants associated with suspended particulate matter followed by data acquired using passive sampling devices.

3.1 Monitoring of trace metals

3.1.1 Trace metal measurements with Diffusive Gradient in Thin film devices (DGTs) and SCF

Figure 3-1 shows the results obtained for Al, Mn, Fe, Ni, Cd, Zn, Cu, and Pb in the Drammenselva River. Panels show total concentration, concentration in the filtered phase and the concentration in filtered & ion-exchanged water in samples collected on the 15th of September and the 13th of October 2008. Horizontal lines show concentrations of DGT labile metal species integrated over 2 deployment times (September 15th – October 13th and October 13th – November 5th). The different colours represent sampling with 2 different types of DGT devices, the results of which will be compared in the section below. Until then, however, the discussion will refer to DGT results represented by red lines, which were obtained using devices of the standard type. The table below shows the chemical speciation of metals calculated using WHAM (Mechanistic Windermere Humic Aqueous Model).

Al, Fe, Mn. These metals are not included in the RID monitoring program. They tend to be represented in the particulate fraction in circum-neutral water in oxic surface water (Davison 1993), and the present results show that their dissolved fractions are significantly smaller than the total concentrations. Most of the Al and Fe that passed through the filter also passed through the cation-exchange cartridge, indicating that colloidal oxides/hydroxides or negatively charged complexes with humic substances dominated the filtered fraction. The dissolved concentrations of Al and Fe were indeed predicted (using WHAM) to be appreciably smaller than the filtered concentrations, owing to supersaturation with respect to solid phases. The finding that DGT labile concentrations of Al and Fe are lower than the filterable concentrations can be explained by slow diffusion and inefficient binding of metals associated with inorganic colloids and humic substances. About half of the dissolved fraction of Mn is retained in the cation exchange cartridge, indicating that some of the Mn is present as cationic species of the divalent oxidation state. The oxidation of divalent Mn occurs at a slow rate (much slower than the oxidation of divalent Fe, for example), explaining why a significant fraction of Mn is often found in the dissolved, cationic fraction [57].

Ni, Cd, Zn. These metals are included in the RID monitoring program. The total concentrations of Cd and Zn are similar to values obtained in 2006 and 2007 while the concentration of Ni is somewhat lower [3]. There are no significant differences between concentrations in total and filtered samples, indicating that the particulate fraction is negligible. Concentrations of Cd and Zn in samples that were passed through both the filter and the ion-exchange cartridge were below the limit of quantification or too variable for meaningful interpretation. Surprisingly, little of the Ni was retained in the cation exchange cartridge, which is also consistent with C_{DGT} being much lower than the filterable concentration. According to model VI, only a small fraction of Ni should be bound by humic substances. The reason for this finding is therefore not clear. There were no clear differences between the filterable fraction of Zn and C_{DGT}. The dissolved fraction of Cd appeared to be larger than C_{DGT}, probably owing to slow diffusion of humic complexes, which were predicted to bind 50% of the dissolved Cd (See Table 3-1).

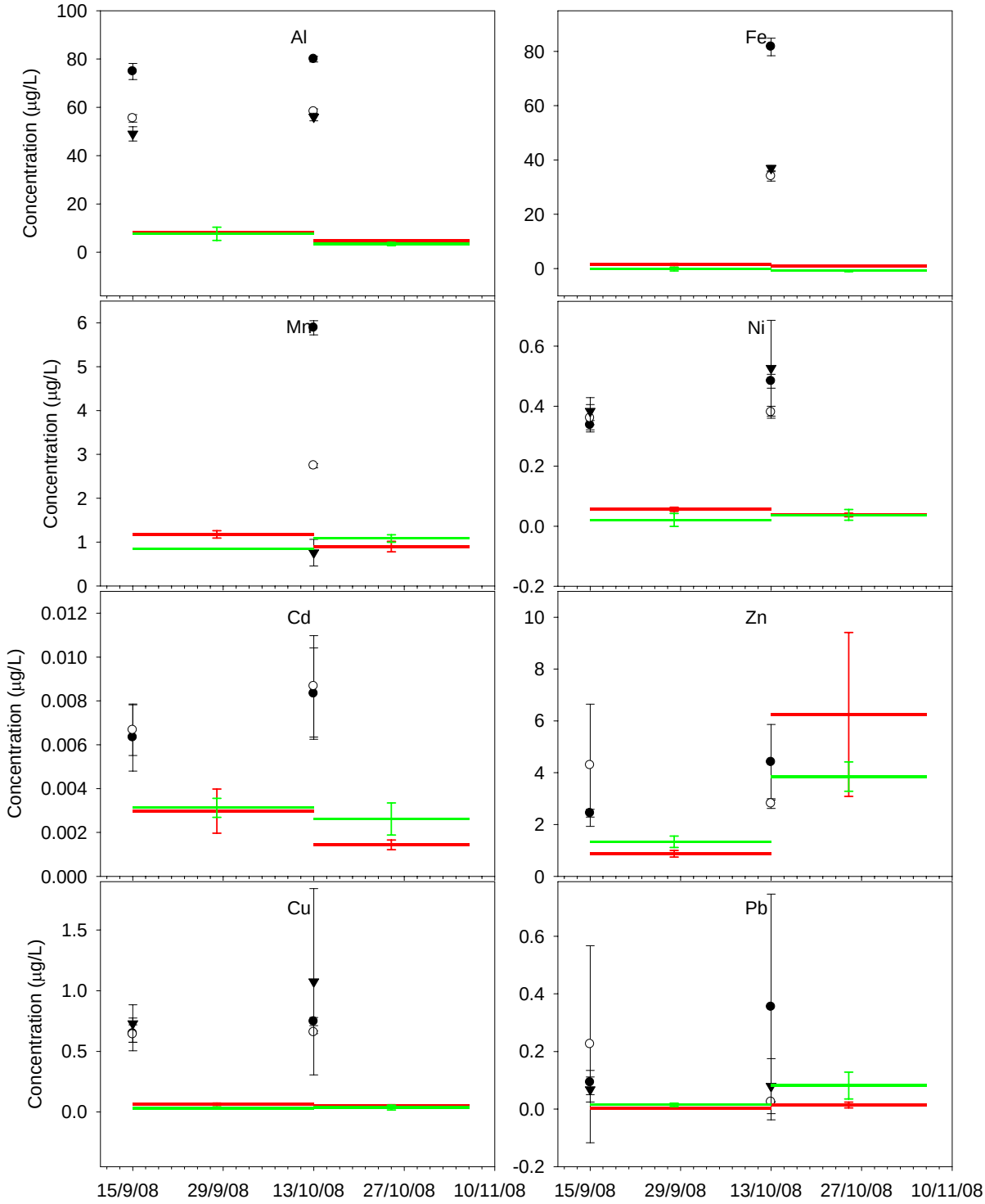

Figure 3-1. Total concentration is presented as filled circles, filtered fraction as open circles, filtered and cation-exchanged fraction as filled triangles, DGT labile fraction obtained with standard DGT devices as red lines, and DGT labile fraction obtained with paper-based sorbent as green lines. Each symbol/line represents the average of 3 replicates and the error bars denote the standard deviation.

Table 3-1. Average concentrations in filtered samples, dissolved concentration (same as filterable concentration for all but Al and Fe (see above)), and the fraction bound to humic substances as calculated by Model VI in WHAM.

	Filterable concentration (µg/L)	Dissolved concentration (µg/L)	Predicted fraction bound to humic substances (percent)
Al	57	16	26
Fe	34	0.33	1
Mn	2.7	2.7	33
Cd	0.010	0.010	50
Zn	3.6	3.6	36
Ni	0.37	0.37	27
Cu	0.65	0.65	100
Pb	0.030	0.030	99

Cu, Pb. The measured total concentrations of these metals are relatively low compared to monitoring data from 2006 and 2007 [3]. However, replicate measurements for Pb were highly variable, implying high measurement uncertainty. This precludes meaningful interpretation of the SCF fractionation results for Pb or comparison with results obtained using DGT. There was no indication of a particulate fraction for Cu (i.e., total and filtered sampled showed similar concentrations). Moreover, the fraction of Cu that passed through the filter also passed through the cation-exhange cartridge. This is not surprising considering the high affinity of humic substances for Cu (see table above), and is also consistent with the finding that C_{DGT} is significantly smaller than the concentration in filtered samples.

3.1.2 Evaluation of SCF fractionation and DGT technique with different sorbent layers

The use of solid-phase extraction cartridges has so far mainly been used for isolation and purification of organic compounds, however, they have several attractive features also for metal speciation studies: they are cheap and disposable; they can be cleaned and rapidly conditioned with buffer and sample solution; the fractionation can be done in the field and is easily combined with filtration to achieve size-charge fractionation (SCF). Moreover, combination with a multi-element determination technique such as ICP-MS allows a wide range of elements to be studied simultaneously. The concept of quantifying the fractions retained by the filter and the ion-exchange cartridge as the difference between the total and filtered fraction and the filtered and filtered & ion-exchanged fraction has both advantages and disadvantages. The advantages are firstly that the problem of cartridge blanks is reduced. Secondly, refraining from elution allows a preconditioning of the cartridge with sample, thus minimising changes in pH which have been previously shown to influence the fractionation [58, 59]. Thirdly, the same cartridge can potentially be used for several samples. The main drawback of determining a fraction as the difference between two other fractions is the difficulty to determine a fraction that is small compared to the other fractions. In this case the uncertainty will be high because a small fraction is calculated as the difference between two much larger numbers, which themselves are prone to uncertainty. This is less of a problem when concentrations are high [60], and the present results show that the method still provides useful information about metal speciation.

DGT results were similar for the two deployment periods except for Zn, which showed higher concentration in the second period (Figure above). Note that this is not reflected in the total or filtered concentration of Zn. More than two grab samples would be required to obtain a representative average concentration when the metal concentration fluctuates [61, 62]. An

important advantage of DGT is the ability to obtain time-averaged concentrations, thus minimising the number of samples required to cover a given time-span. This attribute could be highly useful for monitoring programs such as RID where the objective is to monitor riverine inputs of selected pollutants to Norwegian coastal waters [63]. However, a difficulty is that one is often interested in the dissolved concentration and not the specific fraction that is collected by DGT samplers. One possibility to overcome this difficulty could be to develop a model for estimating the dissolved fraction based on the DGT labile fraction. The present study indicates that this could be possible, considering that results (except for Ni) could be explained by comparison with predictions produced by WHAM. Uncertainties associated with such an approach would probably be relatively low for metals like Cd and Zn whose DGT labile fractions are relatively large compared to the dissolved fractions.

Results obtained with DGTs containing the standard sorbent layer comprised by Chelex beads embedded in a polyacrylamide layer and DGTs containing the paper-based sorbent proposed by Li et al. (2002) were generally very similar for the metals considered here. The paper-based sorbent layer is easier to handle compared to a hydrogel and may offer practical advantages. The good agreement also paves the way for further tests with fully paper-based DGTs as proposed in the literature [64], where the diffusion layer too is replaced by a filter membrane.

3.1.3 Measurement of Hg in the Drammenselva and Akerselva using DGTs

Extracts from standard DGT devices deployed in the Drammenselva were analysed for Hg. Blank contamination was observed and no pattern in Hg accumulation in exposed samplers could be observed.

The opportunity of other work where Hg concentration in river water may be higher was taken. Therefore, three types of DGTs (triplicates) were exposed in the Akerselva to compare Hg accumulation. The two other types of DGTs were made of an agarose diffusive gel to lower interaction between Hg and the gel and either a standard chelex receiving phase or a spheron-thiol resin with higher capacity for Hg species (including complexes) [55, 56]. These DGTs were deployed from December 2008 until January 2009 and results are not directly comparable to those for standard DGTs.

Figure 3-2 shows blank contamination was high (solvent blanks were low and therefore Hg is from the samplers). Accumulation of Hg in sampler at site 2 was significant and Hg must have been significantly higher in order to be detected by standard DGTs (Figure 3-2). Levels in samplers exposed at site 3 are slightly higher than Hg measured in blanks.

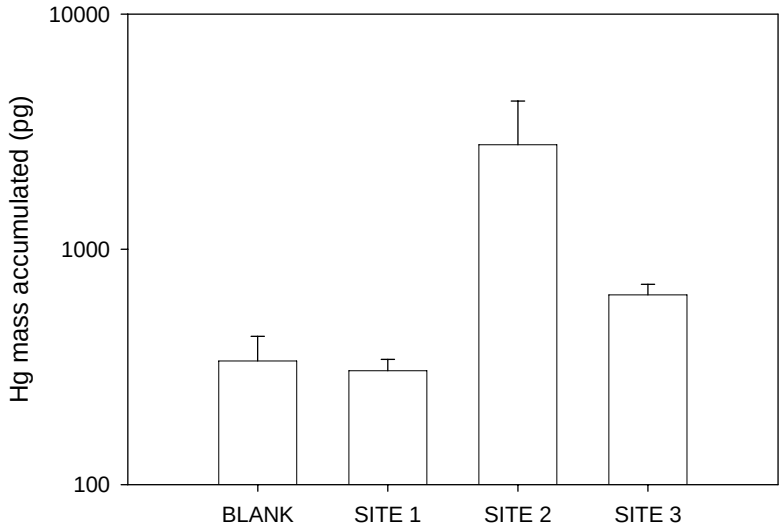

Figure 3-2. Hg masses (pg) in blank samplers and in those found in samplers deployed at three stations in the Akerselva (Oslo). Note: these are for the standard version of DGTs (chelex resin).

Blank contamination also appears to be an issue for the two other types of devices (Figure 3-3). Results shown below appear very variable especially for the version using an agarose gel and a chelex receiving phase. Slight Hg accumulation can be seen in samplers made with a spheron-thiol resin deployed at site 2.

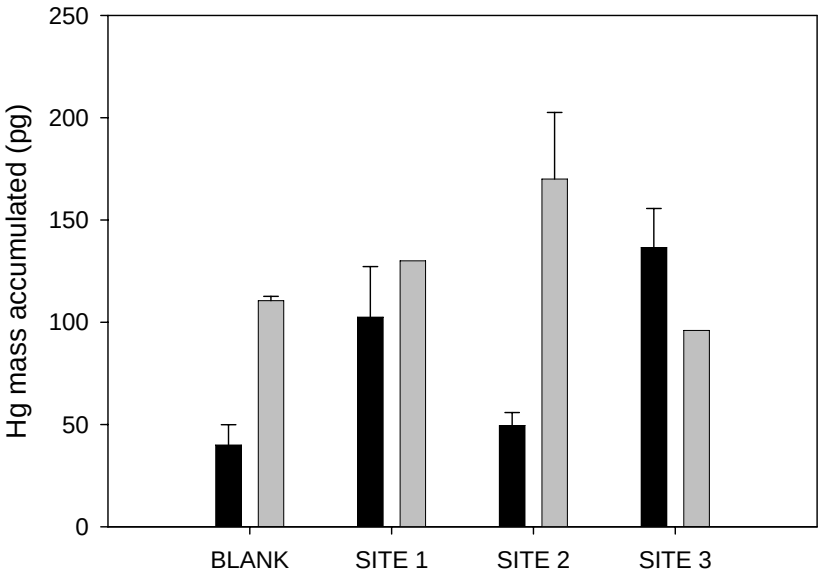

Figure 3-3. Hg masses (pg) in two types of DGT samplers. Data is for blank samplers and in those found in samplers deployed at three stations in the Akerselva (Oslo). Both types of samplers are made of an agarose diffusive gel layers but one use a conventional chelex resin (black bars) and the other is made of a spheron-thiol resin supposed to have a higher capacity for Hg. Note that this samplers were not deployed simultaneously to the conventional version of DGTs.

Finally, diffusive gels from all types of samplers were also extracted (with a similar procedure to that used for the receiving phases). Levels of Hg in diffusive gels are not negligible in blanks and higher levels in exposed samplers compared with blanks can generally be seen (Figure 3-4).

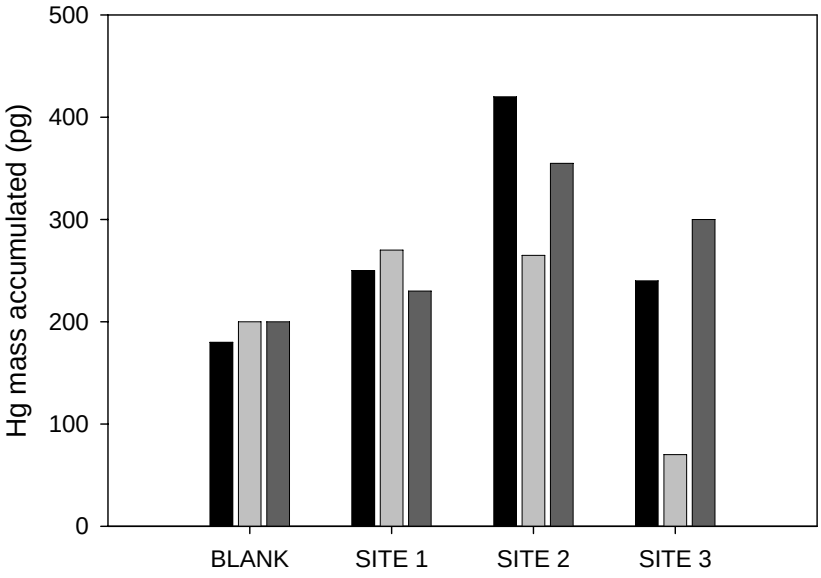

Figure 3-4. Hg masses (pg) in the diffusive gel of three types of DGT samplers. Data is for blank samplers and in those found in samplers deployed at three stations in the Akerselva (Oslo). Black bars are found the polyacrylamide gel of the standard version of DGT while the remaining bars are for the agarose gel of those made assembled with a chelex resin (light grey bars) and a spheron-thiol resin (dark grey bars).

3.2 Screening for pharmaceutical compounds

Polar Chemical Integrative Samplers were extracted and analysed for a series of pharmaceutical compounds (see Table 3-2). Out of all the compounds listed in the table below, only paracetamol and carbamazepine were detected. The mass of paracetamol accumulated varied between 20 and 43 ng per device. Carbamazepine was above LOD but below LOQ. Thorough understanding of the uptake of contaminants into POCIS devices is currently lacking and therefore trying to predict accurately concentrations in water from masses accumulated is difficult. For pharmaceuticals, the range of uptake rates 0.04-1.0 L d^{-1} may be used to semi quantitatively estimate concentrations of paracetamol [53]. This is equivalent to a range of concentrations between 1 and 30 ng L^{-1}.

Table 3-2. Masses of pharmaceutical compounds accumulated during a 28 day exposure of POCIS passive sampling devices in the Drammenselva.

	Concentration in POCIS (ng $device^{-1}$)			
	#1	#2	#3	Blank
Paracetamol	42,8	26,7	20,3	<LoD
Naproxen	<LoD	<LoD	<LoD	<LoD
Propranolol	<LoD	<LoD	<LoD	<LoD
Carbamazepine	<LoQ	<LoQ	<LoQ	<LoD
Amitriptyline	<LoD	<LoQ	<LoD	<LoD

Spiramycin	<LoD	<LoD	<LoD	<LoD
Morphine	<LoD	<LoD	<LoD	<LoD
Sertraline	<LoD	<LoD	<LoD	<LoD
Warfarin	<LoD	<LoD	<LoD	<LoD
Tamoxifen	<LoD	<LoD	<LoD	<LoD
Atorvastatin	<LoD	<LoD	<LoD	<LoD
Diclofenac	<LoD	<LoD	<LoD	<LoD

3.3 Monitoring of contaminants associated to suspended particulate matter

3.3.1 Measurements with time-integrative suspended sediment samplers

With a deployment time of over 3 weeks, amounts of SPM recovered from these samplers were relatively low (a few grams wet weight). The main reason for that is the low level of SPM in the Drammenselva. This has direct implications for the limits of detection that can be achieved with such sampling procedure. Limits of detection were in the range 0.5-10 ng g^{-1} dry weight for PCBs and certain organochlorines. Concentrations of hexachlorobenzene (HCB) in the two replicate samples (each of them made from two samplers) were in the same range and close. Most remaining analytes were below limits of detection (Table 3-3).

Table 3-3. Concentration of PCBs and organochlorines (ng g^{-1} dw) measured on 2 suspended particulate matter samples collected with the integrative suspended sediment sampler.

	Concentration in SPM (ng g^{-1} dw)	
Analyte ID	Sample 1	Sample 2
CB28	<1.0	<1.1
CB52	<2	<10
CB101	*i*	*i*
CB118	<0.7	**1.7**
CB105	<0.7	<2
CB153	<1	<3
CB138	<1	<2.5
CB156	<0.5	<0.7
CB180	<0.9	<1
CB209	<0.5	<1
PeCB	<0.8	<1.6
α-HCH	<1	<1
HCB	**0.93**	**1.6**
γ-HCH	<0.5	**1.1**
p,p'-DDE	<0.8	<1
p,p'-DDD	<1	<1
i: interferences on the chromatogram		

For PBDEs, limits of detection were in the range 0.2-13 ng g^{-1} dry weight. Such sampling procedure allowed the detection of very low levels of BDE47 and BDE209 with sample 2 also showing the presence of BDE99. A factor of three between concentrations measured in the two samples is not unreasonable when taking into account the time integrative nature of the

sampling and the amount of processing required prior to SPM extraction and analysis. The mass of SPM of sample 2 was lower than that of sample 1 resulting in higher limits of detections (Table 3-4).

Table 3-4. Concentration of PBDEs (ng g^{-1} dw) measured on 2 suspended particulate matter samples collected with the integrative suspended sediment sampler.

	Concentration in SPM (ng g^{-1} dw)	
Analyte ID	Sample 1	Sample 2
BDE28	<0.2	<0.8
BDE49	<0.2	<0.8
BDE47	**0.29**	**0.95**
BDE66	<0.2	<0.5
BDE71	<0.2	<0.5
BDE77	<0.2	<0.6
BDE85	<0.3	<0.6
BDE99	<0.3	**1.6**
BDE100	<0.3	<1
BDE119	<0.2	<1
BDE138	<0.3	<2
BDE153	<0.3	<1.2
BDE154	<0.3	<1.1
BDE183	<0.3	<8
BDE196	<3	<13
BDE205	<0.6	<3
BDE209	**6**	**18**
i: interferences on the chromatogram		

Using data on SPM levels recorded in the Drammenselva during this fieldwork, it is possible to estimate "whole water" concentrations to be used for the calculation of fluxes of contaminants. This allows us to calculate "whole water" concentrations with effective limits of detection in the range 0.6-12 pg L^{-1} based on contaminants associated with the particular phase. Concentrations of HCB in the two samples were between 1 and 2 pg L^{-1} of water in the particulate phase (Table 3-5).

Table 3-5. SPM-associated concentration of PCBs and organochlorines in water (pg L^{-1}) measured on 2 suspended particulate matter samples collected with the integrative suspended sediment sampler.

	Concentration in water (pg L^{-1})	
Analyte ID	Sample 1	Sample 2
CB28	<1.2	<1.3
CB52	<2.3	<12
CB101	*i*	*i*
CB118	<0.8	**2.0**
CB105	<0.8	<2.3
CB153	<1.2	<3.5
CB138	<1.2	<2.9
CB156	<0.6	<0.8

CB180	<1.1	<1.2
CB209	<0.6	<1.2
PeCB	<0.9	<1.9
α-HCH	<1.2	<1.2
HCB	**1.1**	**1.9**
γ-HCH	<0.6	**1.3**
p,p'-DDE	<0.9	<1.2
p,p'-DDD	<1.2	<1.2
i: interferences on the chromatogram		

This calculation allows the determination of limits of detection for PBDEs in the range 0.2-15.2 pg L^{-1}. Concentrations of BDE47 and BDE209 were around 1 and 7-21 pg L^{-1}, respectively (Table 3-6).

Table 3-6. SPM-associated concentration of PBDEs in water (pg L^{-1}) measured on 2 suspended particulate matter samples collected with the integrative suspended sediment sampler.

	Concentration in water (pg L^{-1})	
Analyte ID	Sample 1	Sample 2
BDE28	<0.2	<0.9
BDE49	<0.2	<0.9
BDE47	**0.3**	**1.1**
BDE66	<0.2	<0.6
BDE71	<0.2	<0.6
BDE77	<0.2	<0.7
BDE85	<0.4	<0.7
BDE99	<0.4	**1.9**
BDE100	<0.4	<1.2
BDE119	<0.2	<1.2
BDE138	<0.4	<2.3
BDE153	<0.4	<1.4
BDE154	<0.4	<1.3
BDE183	<0.4	<9.4
BDE196	<3.5	<15.2
BDE205	<0.7	<3.5
BDE209	**7.0**	**21.1**
i: interferences on the chromatogram		

Overall, most data for PBDEs, PCBs and organochlorines appears below limits of detection despite calculated limits of detection in the low pg L^{-1} range. Detection of HCB, BDE47 and BDE2009 in both samples was predictable since these are ubiquitous, and concentrations were in the same range.

3.3.2 Measurements with the continuous-flow centrifuge

Centrifugation was conducted on three occasions and this resulted in 3 samples for analysis. These were extracted and analysed for PBDEs, PCBs and organochlorines. Analysis for

organochlorines and PCBs showed relatively variable results with the detection of the highest number of analytes in sample 3 (Table 3-7). These were CB118, CB153, CB138, HCB, and DDT degradation products. All were close to limits of detection and in a similar range close to 1 ng g^{-1} dry weight of SPM. HCB, CB118 and lindane were detected in samples one and two. HCB concentrations in all three samples were between 1 and 2 ng g^{-1} dry weight of SPM. This range is similar to HCB concentrations measured with the time-integrative SPM sampler.

Table 3-7. Concentration of PCBs and organochlorines (ng g^{-1} dw) measured on 3 suspended particulate matter samples collected with the continuous flow centrifuge.

	Concentration in SPM (ng g^{-1} dw)		
Analyte ID	Sample 1	Sample 2	Sample 3
CB28	<2	<3	<1.3
CB52	<6	<7	<3
CB101	*i*	*i*	i
CB118	**2.9**	<3	**1.3**
CB105	<2	<2	<0.7
CB153	<3	<5	**1.3**
CB138	<2.5	<2	**1.7**
CB156	<1	<2	<0.5
CB180	<1	<2	**0.83**
CB209	<1	<2	<0.5
PeCB	<1.6	<1.6	<0.8
α-HCH	<1	<1	<1
HCB	**1.8**	**2.1**	**1.6**
γ-HCH	**2**	**2.1**	<0.5
p,p'-DDE	<1.3	<2	**1.4**
p,p'-DDD	<1	<3	**1.2**
i: interferences on the chromatogram			

As shown in Table 3-8, no PBDEs were detected in sample 3 while BDE47, BDE99 and BDE209 were detected in sample 1 (sample 2 for BDE209). Concentrations of BDE209 are in a similar order of magnitude as those measured with the time-integrative suspended particulate sampler. Here, concentrations were 36 and 12 ng g^{-1} for samples 1 and 2, respectively.

Table 3-8. Concentration of PBDEs (ng g^{-1} dw) measured on 3 suspended particulate matter samples collected with the continuous flow centrifuge.

	Concentration in SPM (ng g^{-1} dw)		
Analyte ID	Sample 1	Sample 2	Sample 3
BDE28	<1	<2.5	<0.2
BDE49	<1	<2	<0.2
BDE47	**2.4**	<1.5	<0.2
BDE66	<0.9	<0.7	<0.2
BDE71	<1	<2.5	<0.2
BDE77	<1	<1.5	<0.2

BDE85	<0.8	<1.1	<0.2
BDE99	**3.4**	<2	<0.2
BDE100	<1.3	<2	<0.2
BDE119	<1.3	<2	<0.2
BDE138	<3	<2.6	<0.2
BDE153	<3	<3	<0.2
BDE154	<1.4	<2	<0.2
BDE183	<10	<15	<1.6
BDE196	<16	<25	<2.5
BDE205	<5	<7	<0.3
BDE209	**36**	**12**	<3
i: interferences on the chromatogram			

Re-calculated "whole water" concentrations of organochlorines and PCBs were all very low and generally between 1 and 4 pg L^{-1} (Table 3-9). Limits of detection based on levels of SPM in water are in the range 0.6 to 8 pg L^{-1}.

Table 3-9. SPM-associated concentration of PCBs and organochlorines in water (pg L^{-1}) measured on 3 continuous-flow centrifuge samples.

	Concentration in water (pg L^{-1})		
Analyte ID	Sample 1	Sample 2	Sample 3
CB28	<2.3	<3.5	<1.5
CB52	<7.0	<8.2	<3.5
CB101	*i*	*i*	*i*
CB118	**3.4**	<3.5	**1.5**
CB105	<2.3	<2.3	<0.8
CB153	<3.5	<5.9	**1.5**
CB138	<2.9	<2.3	**2.0**
CB156	<1.2	<2.3	<0.6
CB180	<1.2	<2.3	**1.0**
CB209	<1.2	<2.3	<0.6
PeCB	<1.9	<1.9	<0.9
α-HCH	<1.2	<1.2	<1.2
HCB	**2.1**	**2.5**	**1.9**
γ-HCH	**2.3**	**2.5**	<0.6
p,p'-DDE	<1.5	<2.3	**1.6**
p,p'-DDD	<1.2	<3.5	**1.4**
i: interferences on the chromatogram			

Resulting "whole water" concentrations of PBDEs were around a few pg L^{-1} for BDE47 and BDE99, while concentrations one order of magnitude higher were calculated for BDE209 (Table 3-10).Limits of detection of particulate matter-associated PBDEs were between 0.2 and 25 pg L^{-1}.

Table 3-10. SPM-associated concentration of PBDEs in water (pg L^{-1}) measured on 3 continuous-flow centrifuge samples.

	Concentration in water (pg L^{-1})		
Analyte	Sample 1	Sample 2	Sample 3

ID			
BDE28	<1	<2.5	<0.2
BDE49	<1	<2	<0.2
BDE47	**2.4**	<1.5	<0.2
BDE66	<0.9	<0.7	<0.2
BDE71	<1	<2.5	<0.2
BDE77	<1	<1.5	<0.2
BDE85	<0.8	<1.1	<0.2
BDE99	**3.4**	<2	<0.2
BDE100	<1.3	<2	<0.2
BDE119	<1.3	<2	<0.2
BDE138	<3	<2.6	<0.2
BDE153	<3	<3	<0.2
BDE154	<1.4	<2	<0.2
BDE183	<10	<15	<1.6
BDE196	<16	<25	<2.5
BDE205	<5	<7	<0.3
BDE209	**36**	**12**	<3
i: interferences on the chromatogram			

A similar range of contaminants was detected and quantified using the continuous-flow centrifuge as was found using the time-integrative suspended particulate sampler. When the sample is collected may have had an impact on the concentrations measured with the continuous flow centrifugation since the source and levels of SPM may vary. Such fluctuations are likely to be integrated when using the suspended sediment sampler. The grain-size distribution of samples collected with the two sampling methodologies may result in differences in concentrations that may be measured.

3.3.3 Monitoring of SPM-associated PFCs

Freeze-dried SPM was extracted for screening for a number of perfluoroalkyl compounds (Table 3-11). Most PFCs were below limits of detection. These were in the range of 5-30 ng g^{-1} dry weight of SPM. Low levels of perfluorobutane sulfonate (PFBS) were detected in two centrifuge samples and one sample from the time-integrative SPM sampler. Concentrations are very close; however these are also very close to limits of detection. Perfluorooctane sulphonamide (PFOSA) was also detected in two samples at a similar concentration as that observed for PFBS.

Table 3-11. PFC concentrations (ng g^{-1} dw) in SPM samples from the time-integrative sediment samplers and continuous flow centrifugation.

Sample number	PFBS	PFHxA	PFHpA	PFOA	PFNA	PFOS	PFOSA
SPM-sampler 1	<10	<20	<30	<5	<30	<20	<10
SPM-sampler 2	15.0	<20	<30	<5	<30	<20	20.5
Centrifuge 1	<10	<20	<30	<5	<30	<20	<10
Centrifuge 2	26.5	<20	<30	<5	<30	<20	19.7
Centrifuge 3	11.5	<20	<30	<5	<30	<20	<10
PFBS= perfluorobutane sulfonate; PFHxA = perfluorohexanoic acid; PFHpA = perfluoroheptanoic acid; PFOA = perfluorooctanoic acid, PFNA = perfluorononanoic acid,							

PFOS = perfluorooctane sulfonate; PFOSA = Perfluorooctane sulphonamide

Taking into account the level of SPM in the Drammenselva at the moment the sampling was undertaken results in calculated water concentrations shown in Table 3-12.

Table 3-12. SPM-associated PFC concentrations (pg L^{-1}) in water measured with the time-integrative sediment samplers and with continuous flow centrifugation.

Sample number	PFBS	PFHxA	PFHpA	PFOA	PFNA	PFOS	PFOSA
SPM-sampler 1	<12	<24	<35	<6	<35.	<24	<12
SPM-sampler 2	17.6	<24	<35	<6	<35.	<24	24.0
Centrifuge 1	<12	<24	<35	<6	<35.	<24	<12
Centrifuge 2	31.0	<24	<35	<6	<35.	<24	23.0
Centrifuge 3	13.5	<24	<35	<6	<35.	<24	<12
PFBS= perfluorobutane sulfonate; PFHxA = perfluorohexanoic acid; PFHpA = perfluoroheptanoic acid; PFOA = perfluorooctanoic acid, PFNA = perfluorononanoic acid, PFOS = perfluorooctane sulfonate; PFOSA = Perfluorooctane sulphonamide							

3.3.4 Large volume water sampling

Large volume water sampling was conducted twice on each of two occasions and this resulted in four filter and polyurethane foam plug samples. A GF/F 0.7 μm filter was used and was assumed to retain all particles larger than this pore size. Such sampling technique allowed the processing and filtration of between 160 to 300 L for each sample. Exact volumes of water that were filtered for each sample are shown in Table 3-13.

Table 3-13. Volumes (L) of river water filtered with the large volume water sampler on 4 sampling occasions.

Sample ID	Collection date	Volume of river water filtered (L)
1	23-Oct	290
2	23-Oct	225
3	05-Nov	163
4	05-Nov	193

Filters and polyurethane foam plugs were extracted by soxhlet and analysed for organochlorines, PBDEs and PCBs. Results are presented below.

3.3.4.1 Measurement of PBDEs with large volume water sampling

Similar PBDEs to those detected in SPM samples from the centrifugation and the time-integrative SPM sampler were observed using large volume water sampling. These were BDE47, BDE99 and BDE209 (and BDE183 detected in 1 sample). Highest concentrations (ng $filter^{-1}$) were observed for BDE209 while those measured for BDE47 and BDE99 were on average over one order of magnitude lower (Table 3-14). All other PBDEs were below limits of detection. LOD values appear in a similar range for most except for sample 3 that seem generally higher.

Table 3-14. PBDE concentration measured in the filter (ng $filter^{-1}$) for the four large volume water samples collected on the 23/10/08 and 05/11/08.

PBDE ID	Concentration (ng $filter^{-1}$)*

	1	2	3	4
BDE8	<0.2	<0.2	<0.6	<0.2
BDE28	<0.07	<0.06	<0.4	<0.06
BDE49	<0.05	<0.05	<0.3	<0.05
BDE71	<0.05	<0.04	<0.3	<0.07
BDE47	**0.05**	**0.07**	**1.70**	**0.19**
BDE66	<0.05	<0.04	<0.2	<0.05
BDE77	<0.03	<0.03	<0.2	<0.03
BDE100	<0.03	<0.03	<0.3	<0.03
BDE119	<0.05	<0.05	<0.2	<0.05
BDE99	**0.12**	**0.09**	**0.30**	<0.05
BDE85	<0.03	<0.03	<0.2	<0.03
BDE154	<0.04	<0.04	<0.2	<0.04
BDE153	<0.05	<0.04	<0.2	<0.05
BDE138	<0.03	<0.03	<0.3	<0.04
BDE183	<0.05	<0.05	**1.07**	<0.06
BDE196	<0.2	<0.2	<0.3	<0.2
BDE205	<0.07	<0.04	<0.3	<0.07
BDE209	**8.4**	**3.3**	**58**	**6.8**
*Use of a 0.7 μm GF/F filter				

The extraction of PUF plugs and analysis for PBDEs resulted similar PBDEs being detected (Table 3-15). However additional PBDEs such as BDE8, BDE49, BDE100 to BDE196 were detected. No simple pattern can really be distinguished. Generally sample four exhibits highest concentrations with for example over 3 and 15 ng of BDE47 and BDE99, respectively extracted per PUF. No BDE209 however was detected in that particular sample.

Table 3-15. PBDE concentration measured in the polyurethane foam plug (PUF) (ng PUF^{-1}) for the four large volume water samples collected on the 23/10/08 and 05/11/08.

PBDE ID	Concentration (ng PUF^{-1})			
	1	2	3	4
BDE8	<0.6	**8.50**	<0.2	<0.2
BDE28	<0.3	<0.6	<0.07	<0.06
BDE49	<0.1	<0.2	<0.03	**0.08**
BDE71	<0.1	<0.2	<0.05	<0.05
BDE47	**0.26**	<0.4	**0.29**	**3.62**
BDE66	<0.1	<0.2	<0.05	**0.10**
BDE77	<0.06	<0.1	<0.03	<0.03
BDE100	<0.04	<0.2	<0.03	**2.61**
BDE119	<0.09	<0.2	<0.05	<0.05
BDE99	<0.12	<0.2	**0.17**	**15.40**
BDE85	<0.05	<0.1	<0.03	**0.95**
BDE154	<0.05	<0.1	<0.03	**1.40**
BDE153	<0.09	<0.4	<0.04	**1.90**
BDE138	<0.07	<0.2	<0.04	**0.30**
BDE183	**0.11**	**0.72**	<0.05	<0.05
BDE196	**0.16**	<0.2	<0.2	<0.2
BDE205	<0.1	<0.1	<0.04	<0.04
BDE209	**2.2**	**2.6**	**1.0**	<0.5

Filters were not weighted prior to use with the large volume water sampler. In addition the operational use of the system results in the shatter of the outside of the filter and prevents from accurately measure the total weight post sampling. This would result in much uncertainty. Since accurate information on the total volume of water filtered by the sampler is available, it is possible to express contaminant concentrations in the particulate and in the dissolved phase with respect to the volume of water.

Apart from data for filter sample 3, BDE47 and BDE209 concentrations in water were in the same range as those measured with the centrifuge and with the time-integrative sampler (Table 3-16). Remaining data appears variable and data for PUF plug sample 4 is surprising since none of these compounds can be seen in the filter, despite their very high affinity for sediment particles and organic matter.

Table 3-16. Filtered and particulate (retained on 0.7 μm filter) concentrations of PBDEs in the water the Drammenselva River (pg L^{-1}) measured by large volume water sampling.

	Concentration in Drammenselva River water (pg L^{-1})							
	Filtered				Particulate			
	1	2	3	4	1	2	3	4
BDE8	<2.1	**37.8**	<1.2	<1.0	<0.7	<0.9	<3.7	<1.0
BDE28	<1.0	<2.7	<0.4	<0.3	<0.2	<0.3	<2.5	<0.3
BDE49	<0.3	<0.9	<0.2	**0.4**	<0.2	<0.2	<1.8	<0.3
BDE71	<0.3	<0.9	<0.3	<0.3	<0.2	<0.2	<1.8	<0.4
BDE47	**0.89**	<1.8	<1.8	**18.8**	**0.17**	**0.31**	**10.4**	**0.98**
BDE66	<0.3	<0.9	<0.3	**0.52**	<0.2	<0.2	<1.2	<0.3
BDE77	<0.2	<0.4	<0.2	<0.2	<0.1	<0.1	<1.2	<0.2
BDE100	<0.1	<0.9	<0.2	**13.5**	<0.1	<0.1	<1.8	<0.2
BDE119	<0.3	<0.9	<0.3	<0.3	<0.2	<0.2	<1.2	<0.3
BDE99	<0.4	<0.9	**1.05**	**79.9**	**0.43**	**0.42**	**1.8**	<0.3
BDE85	<0.2	<0.4	<0.2	**4.9**	<0.1	<0.2	<1.2	<0.2
BDE154	<0.2	<0.4	<0.2	**7.3**	<0.1	<0.2	<1.2	<0.2
BDE153	<0.3	<1.8	<0.3	**9.9**	<0.2	<0.2	<1.2	<0.3
BDE138	<0.2	<0.9	<0.3	**1.6**	<0.1	<0.1	<1.8	<0.2
BDE183	**0.39**	**3.20**	<0.3	<0.3	<0.2	<0.2	**6.6**	<0.3
BDE196	**0.55**	<0.9	<1.2	<1.0	<0.7	<0.9	<1.8	<1.0
BDE205	<0.3	<0.4	<0.3	<0.2	<0.2	<0.2	<1.8	<0.4
BDE209	**7.6**	**11.6**	**6.1**	<2.6	**29.0**	**14.7**	**356**	**35.3**

In order to establish whether concentrations measured here are realistic, data from filters and from PUF plugs may be used to calculate approximate particulate organic matter-water partition coefficients for PBDE for which both the filtered and particulate concentrations are above limits of detection. These are plotted on Figure 3-5 as a function of log K_{OW}. In addition, data for which only one or the other piece of data was available were also plotted on the figure below. Log K_{OC} values vary between 6 and 9 while estimates based on 1 limit of detection are in the range 4.5 and 8.5. As expected, these values appear to increase with increasing log K_{OW}.

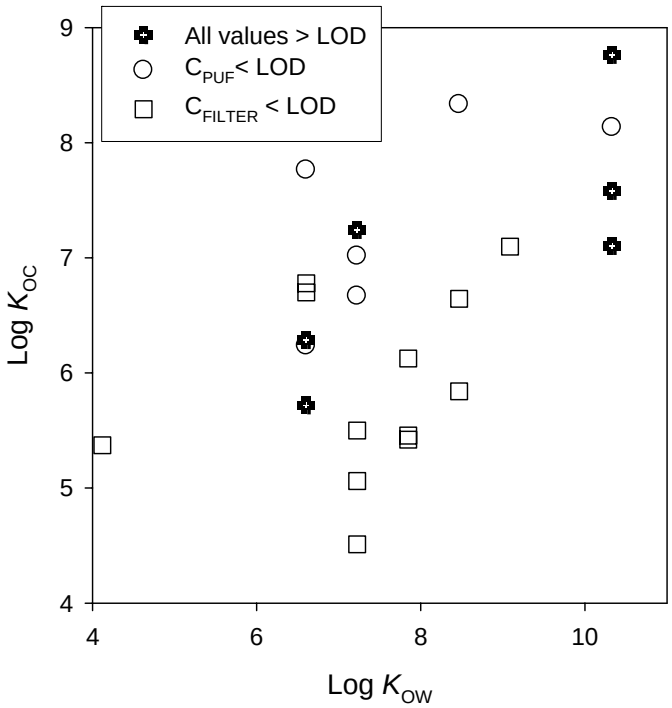

Figure 3-5. Relationship between estimated logarithm of particulate organic carbon-water partition coefficients (log K_{OC}) and logarithm of octanol-water partition coefficients (log K_{OW}) for a range of PBDEs based on large volume water sampling data for the Drammenselva River.

3.3.4.2 Measurement of organochlorines and PCBs with large volume water sampling

Extracts from the filters and from the PUF plugs were also analysed for a series of PCBs and for organochlorine insecticides (Table 3-17). The analysis of the four filters allowed detection of CB28, CB118, CB153, CB138, CB180, *p,p'*-DDE and *p,p'*-DDT, the last three detected in all four filter samples. In addition concentrations of CB180, *p,p'*-DDE, *p,p'*-DDT were in a similar range for all four samples. In most cases, analytes that were detected in the filter are those with highest log K_{OW}s.

Table 3-17. Organochlorine and PCB concentrations measured in the filter (ng filter^{-1}) for the four large volume water samples collected on the 23/10/08 and 05/11/08.

	Concentration (ng filter^{-1})*			
	1	2	3	4
CB28	<0.5	**0.60**	<0.3	**0.45**
CB52	<0.3	<0.3	<0.3	<0.3
CB101	*i*	*i*	*i*	*i*
CB118	<0.2	<0.2	<0.2	**0.42**
CB105	*i*	*i*	*i*	*i*
CB153	<0.3	<0.3	<0.3	**0.34**
CB138	<0.3	<0.3	<0.3	**0.68**
CB156	<0.2	<0.2	<0.2	<0.2
CB180	**0.12**	**0.11**	**0.11**	**0.25**

CB209	<0.2	<0.2	<0.2	<0.2
PeCB	<0.6	<5	<2	<4
α-HCH	<0.3	<0.3	<0.3	<0.3
HCB	<0.5	<0.5	<0.5	<0.5
γ-HCH	<1	<1	<1	<1
p,p'-DDE	**0.25**	**0.29**	**0.40**	**0.72**
p,p'-DDD	<0.3	<0.3	<0.3	**0.38**
p,p'-DDT	**2.3**	**1.7**	**2.0**	**3.9**
*Use of a 0.7 µm GF/F filter *i*: interferences on the chromatogram				

In contrast with the data above, Table 3-18 shows that most of the analytes detected in the PUF plugs were mostly the least hydrophobic ones: CB28, CB52, CB118, pentachlorobenzene, hexachlorobenzene and HCH isomers. In all cases, data from the four water samples appear very consistent. For all these analytes, relative standard deviations of the four measurements are between 19 and 28 % with one value at 44 %. This is highly encouraging especially when taking into account that volumes of the different samples were relatively different.

Table 3-18. Organochlorine and PCB concentrations measured in the polyurethane foam plug (ng PUF^{-1}) for the four large volume water samples collected on the 23/10/08 and 05/11/08.

	Concentration (ng PUF^{-1})			
	1	2	3	4
CB28	**6.4**	**9.3**	**6.22**	**6.05**
CB52	**9.4**	**17**	**7.42**	**7.62**
CB101	<1.5	<1	<2	<2
CB118	<0.6	<1	<0.6	**0.48**
CB105	*i*	*i*	*i*	*i*
CB153	<0.3	<0.3	<0.3	<0.3
CB138	<0.6	<0.9	<0.4	<0.4
CB156	<0.6	<0.7	<0.3	<0.3
CB180	<0.6	<0.7	<0.3	<0.3
CB209	<0.3	<0.3	<0.3	<0.3
PeCB	<0.5	<1	**1.99**	**2.87**
α-HCH	**2.1**	**2.8**	**1.86**	**2.00**
HCB	**6.9**	**9.8**	**5.37**	**5.93**
γ-HCH	**3.9**	**5.4**	**3.01**	**3.13**
p,p'-DDE	<1,5	<0,4	<0,4	<0,4
p,p'-DDD	<0,8	<0,7	<0,7	<0,7
p,p'-DDT	<4	<4	<3	<3
i: interferences on the chromatogram				

Similar to the data transformation undertaken for PBDEs, the PCB and organochlorine data was converted to pg of contaminant in the particulate or filtered phase per volume of water. Limits of detections for PCBs and organochlorines are in the range 0.7 to 23 pg L^{-1} depending on the analyte of interest. Calculated concentrations in the particulate phase are in the range 0.4 to 3.7 pg L^{-1} for PCBs. In the filtered phase, concentrations of less hydrophobic compounds are generally one order of magnitude higher than those for more hydrophobic

compounds in the particulate phase. Concentrations of CB28 and CB52 were between 22 and 74 pg L^{-1} in the filtered fraction. HCB concentrations were measured in the range 24-44 pg L^{-1} (Tables 3-19 and 3-20).

Table 3-19. Organochlorine and PCB concentrations measured in the particulate phase (pg L^{-1}) for the four large volume water samples collected on the 23/10/08 and 05/11/08.

	Concentration (pg L^{-1})*			
	1	2	3	4
CB28	<1.7	**2.7**	<1.8	**2.3**
CB52	<1.0	<1.3	<1.8	<1.6
CB101	*i*	*i*	*i*	*I*
CB118	<0.7	<0.9	<1.2	**2.2**
CB105	*i*	*i*	*i*	*I*
CB153	<1.0	<1.3	<1.8	**1.8**
CB138	<1.0	<1.3	<1.8	**3.5**
CB156	<0.7	<0.9	<1.2	<1.0
CB180	**0.4**	**0.5**	**0.7**	**1.3**
CB209	<0.7	<0.9	<1.2	<1.0
PeCB	<2.1	<23	<13	<21
α-HCH	<1.0	<1.3	**1.8**	**1.6**
HCB	<1.7	<2.2	<3.1	<2.6
γ-HCH	<3.4	<4.4	<6.1	<5.2
p,p'-DDE	**0.8**	**1.3**	**2.5**	**3.7**
p,p'-DDD	<1.0	<1.3	<1.8	**2.0**
p,p'-DDT	**7.9**	**7.7**	**12.0**	**20.4**
*Use of a 0.7 μm GF/F filter *i*: interferences on the chromatogram				

Table 3-20. Organochlorine and PCB concentrations measured in the filtered phase (pg L^{-1}) for the four large volume water samples collected on the 23/10/08 and 05/11/08.

	Concentration (pg L^{-1})*			
	1	2	3	4
CB28	**21.9**	**41.1**	**38.2**	**31.4**
CB52	**32.3**	**73.9**	**45.6**	**39.5**
CB101	<5.2	<4.4	<12.3	<10.4
CB118	<2.1	<4.4	<3.7	**2.5**
CB105	*i*	*i*	*i*	*i*
CB153	<1.0	<1.3	<1.8	<1.6
CB138	<2.1	<4.0	<2.5	<2.1
CB156	<2.1	<3.1	<1.8	<1.6
CB180	<2.1	<3.1	<1.8	<1.6
CB209	<1.0	<1.3	<1.8	<1.6
PeCB	<1.7	<4.4	12.2	14.9
α-HCH	**7.3**	**12.3**	**11.4**	**10.4**
HCB	**23.7**	**43.6**	**33.0**	**30.8**
γ-HCH	**13.3**	**23.9**	**18.5**	**16.2**
p,p'-DDE	<5.2	<1.8	<2.5	<2.1
p,p'-DDD	<2.8	<3.1	<4.3	<3.6

p,p'-DDT	<14	<18	<19	<16
*Use of a 0.7 µm GF/F filter *i*: interferences on the chromatogram				

When concentrations in the filtered and particulate fractions are both above limits of detection, it becomes possible to calculate particulate organic carbon-normalised partition coefficients for these compounds. Only 3 analytes met such requirements. It is interesting to note that values of log K_{OC} are close to log K_{OW} values. When either the filtered or particulate fraction was < limits of detection, these were also plotted. On Figure 3-6, it can seen that for analytes > log K_{OW} 5.5-6, log K_{OC}s are likely to be higher than 6.5 while for those with log K_{OW} < 6.0, log K_{OC}s are likely to be lower than 5.5-7.0.

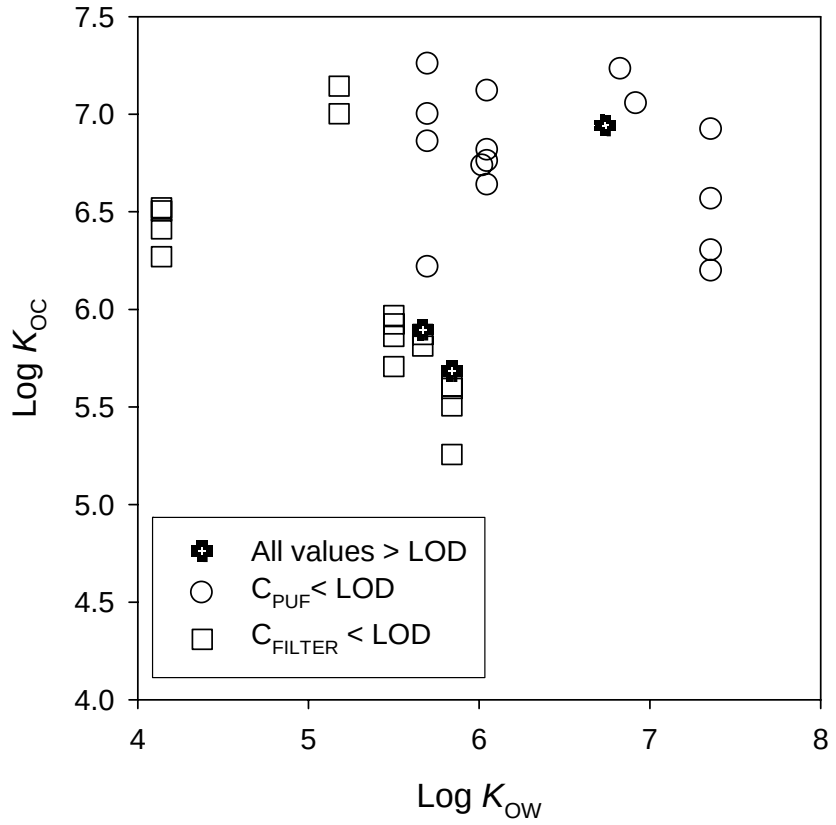

Figure 3-6. Relationship between estimated logarithm of particulate organic carbon-water partition coefficients (log K_{OC}) and logarithm of octanol-water partition coefficients (log K_{OW}) for a range of organochlorines and PCBs based on large volume water sampling data for the Drammenselva River.

3.4 Monitoring of nonpolar organic substances with passive samplers

3.4.1 Performance reference compound (PRC) data

Performance reference compounds are generally used to estimate contaminant exchange rates or kinetics between the sampler and water. This allows estimation of analyte uptake rates *in-situ* [7, 9]. The reason for this is the isotropic nature of both the uptake and offload for a specific analyte. Analytes for which the concentration in the sampler approaches equilibrium

with that in the water are usually characterised by significant if not complete offload of performance reference compounds with similar log K_{OW}. Negligible PRC dissipation is generally indicative of contaminants in the linear phase of uptake. For commonly used passive sampler exposure times, the threshold between these two regimes can be found for log K_{OW} between 4.5 and 5.0.
The use of multiple PRCs ensures that the range of regimes (equilibrium vs. integrative sampling and water boundary vs. membrane controlled uptake regimes) are covered. The range of PRCs with log K_{OW} in the range 4-7 generally enables to establish whether kinetics of uptake into the sampler is controlled by transfer in the membrane or by transfer across the water boundary layer at the surface of the sampler (the size/thickness of this layer depends on hydrodynamics around the sampler).

The overall resistance to mass transfer ($1/k_O$) into the samplers can be expressed as the sum of the water and membrane-side resistances to mass transfer:

$$\frac{1}{k_O} = \frac{\delta_W}{D_W} + \frac{\delta_M}{K_{MW} D_M}$$

with δ_W and δ_M the boundary and membrane layer thicknesses (m), and D_W and D_M (m^2 s^{-1}) analyte diffusion coefficients in water and the membrane, respectively.

Amounts of analytes absorbed by the samplers follow a first-order approach to equilibrium:

$$N = K_{SW}\, V\, C_{TWA} \left[1 - \exp(-k_e t)\right]$$

where N is the amount of analyte absorbed (ng), K_{SW} the sampler-water partition coefficient (L L^{-1}), V the volume of the sampler (L), k_e the exchange rate constant (h^{-1}), t the exposure time (h) and C_{TWA} is in ng L^{-1}.

PRC dissipation also follows first-order kinetics:

$$N_{PRC} = N_{0,PRC} \left[1 - \exp(-k_e t)\right]$$

where $N_{O,PRC}$ and N_{PRC} are PRC masses in the samplers prior to and following exposure, respectively and where k_e is given by:

$$k_e = \frac{k_O A}{K_{SW} V} = \frac{R_S}{K_{SW} V}$$

where k_O is the overall mass transfer coefficient, A the surface area of the sampler (cm^2), V the volume of the sampler (cm^3) and R_S the analyte uptake rates (L d^{-1}).

PRC offload rates, $k_{e,}$ were calculated for the two exposure periods and for all three samplers and their statistical significance tested using a procedure described previously [12]. Data is shown on Figure 3-7. Only data exhibiting significant offload was used thereafter. For SPMD interestingly, it was possible to used d_{12}-chrysene and d_{12}-benzo[*e*]pyrene data for the 51 day exposure since offload was significant for this exposure. These PRCs are not generally used since shorted exposure times are commonly used.

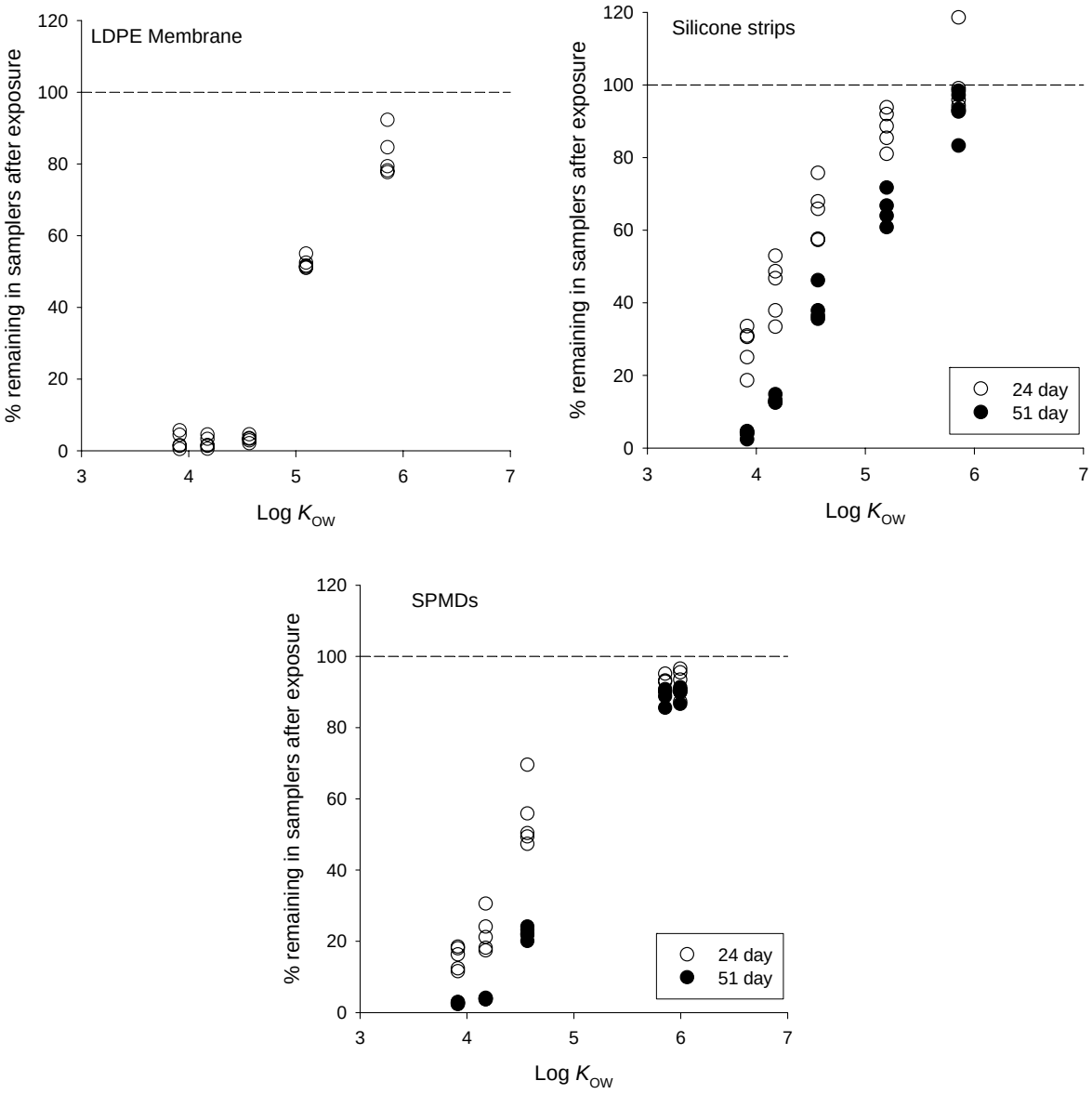

Figure 3-7. Percentage of performance reference compounds remaining in LDPE membranes, silicone strips and SPMDs following 24 and 51 day exposures (3-5 replicates were available for each PRC, hypothetical 100 % line is drawn).

Since the configurations of the devices differed in terms of thicknesses and since k_e is proportional to V/A, offload rates were normalised to this ratio [8]. The relationship between k_eV/A values for 24 and 51 day exposures and log K_{OW} and log K_{SW} is presented here. The spread of the data across the range of samplers is close to or less than 0.5 of a log unit and there appears to be a plateau for PRCs with log K_{OW} ~ 4 for SPMD and LDPE membranes. This plateau is indicative of membrane-controlled mass transfer into the samplers while for more hydrophobic analytes it is expected that transfer across the diffusive boundary layer at the surface of the samplers controls their uptake. Higher analyte diffusion coefficients in silicone significantly reduce the resistance to mass transfer in the membrane and this is the reason why it appears that the silicone data does not exhibit such plateau [19, 20] (See Figures 3-8 and 3-9).

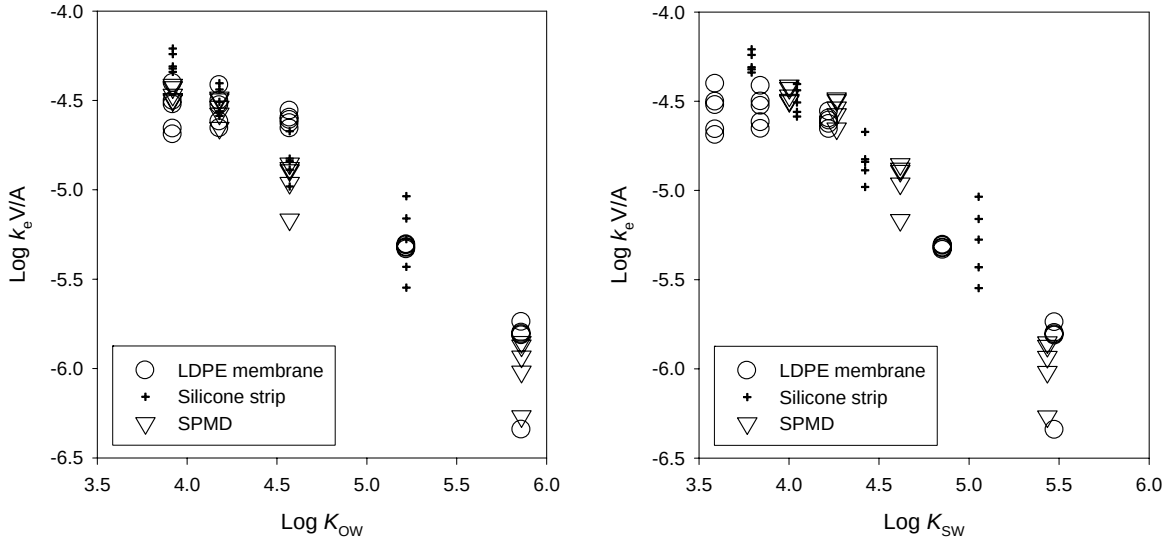

Figure 3-8. Performance reference compound dissipation rates normalised to sampler surface area (A) to volume (V) ratio (cm h^{-1}) versus log K_{OW} or log K_{SW} for a 24 day exposure of LDPE membranes, silicone strips and SPMDs in the Drammenselva (5 replicate per PRC; only data for which dissipation was significant was included).

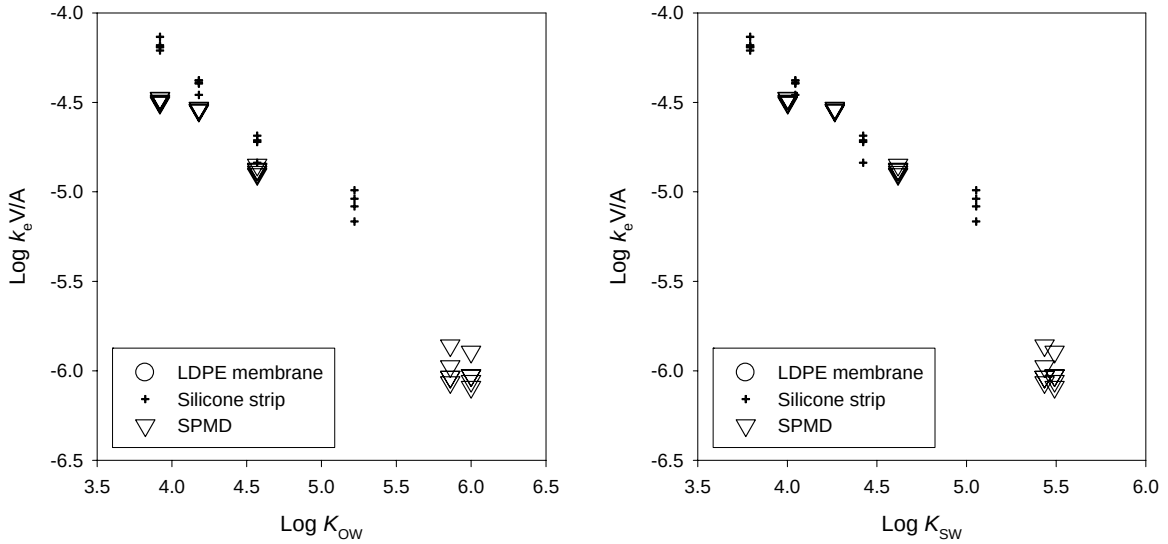

Figure 3-9. Performance reference compound dissipation rates normalised to sampler surface area (A) to volume (V) ratio (cm h^{-1}) versus log K_{OW} or log K_{SW} for a 51 day exposure of silicone strips and SPMDs in the Drammenselva (5 replicate per PRC; only data for which dissipation was significant was included).

Offload rates for PRCs under water boundary layer controlled uptake were plotted as a function of log K_{OW}. Excellent linear relationships between log k_e and log K_{OW} were obtained (Figure 3-10). In addition, the slope of decrease exhibited is very similar for all samplers, irrespective of the material used [19, 20].

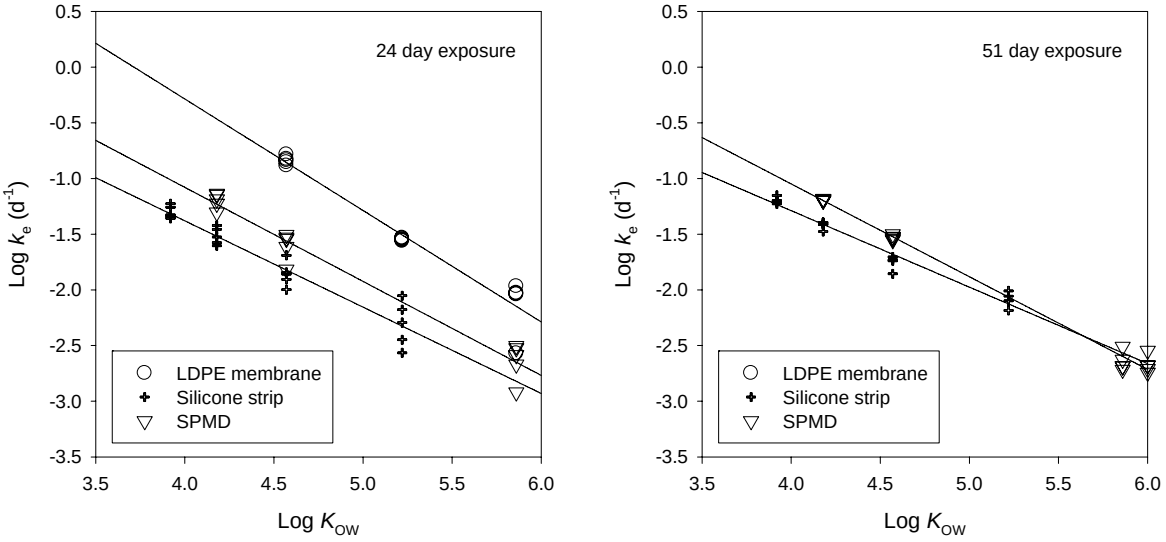

Figure 3-10. First-order performance reference compound dissipation rates, k_e (d^{-1}) for LDPE membranes, silicone strips and SPMD exposed in the Drammenselva for 24 and 51 days (data not included in this graph comprise (a) PRC for which offload was not significant in comparison with control samplers and (b) PRC that were not under water boundary layer controlled uptake; in most cases 5 replicate were available for each exposure and each PRC).

Linear regressions were analysed. Slopes for silicone samplers and SPMD were generally similar (Table 3-21). In both cases, slopes obtained for 24 day exposure were slightly lower than those obtained for the 51 day exposure. Slope for the 24 day exposure of LDPE membranes were steeper than those obtained with silicone strips and SPMDs. Intercepts did not vary much with exposure time and were different for the various sampler materials. Excellent R^2 and standard error values were obtained.

Table 3-21. Summary of results of linear regression of log k_e vs. log K_{OW} for PRC compounds under water boundary layer controlled uptake.

Sampler	Exposure	*a**	*b**	se**	R^2	n***
LDPE membrane	24 days	-1.001	3.72	0.07	0.989	15
	51 days	No samplers exposed				
Silicone strip	24 days	-0.775	1.72	0.06	0.988	20
	51 days	-0.687	1.46	0.04	0.988	18
SPMD	24 days	-0.844	2.30	0.05	0.979	15
	51 days	-0.833	2.28	0.02	0.977	20

*log $k_e = a \log K_{OW} + b$
**standard error of the slope *a*
***number of data points

The aim here was to produce samplers with similar surface areas and dimensions/configuration so that they could be exposed in the river in a very similar way. This reduces possibilities of different water turbulences around the different types of samplers. The data shown above generally confirms this, although the LDPE membrane data appears slightly different to the data from other sampler types. This could be corrected based on the volume of the sampler.

Uptake into the samplers is generally linear or integrative until the concentration in the sampler reaches 50 % of the equilibrium concentration. In other words, PRC elimination rates may be used to predict the amount of time required for the concentration of an analyte in a sampler to reach equilibrium with that in the water:

$$t_{50} = \ln 2 / k_e$$

As shown on Figure 3-11, for silicone strips and SPMD samplers, the limit for integrative sampling to be achieved is between 10 and 20 days for analytes with log K_{OW} < 4.5. For analytes with log K_{OW} ~ 5, time limits are close to 100 days. Those for LDPE membranes are lower generally reflecting the significantly smaller volume of the sampler.

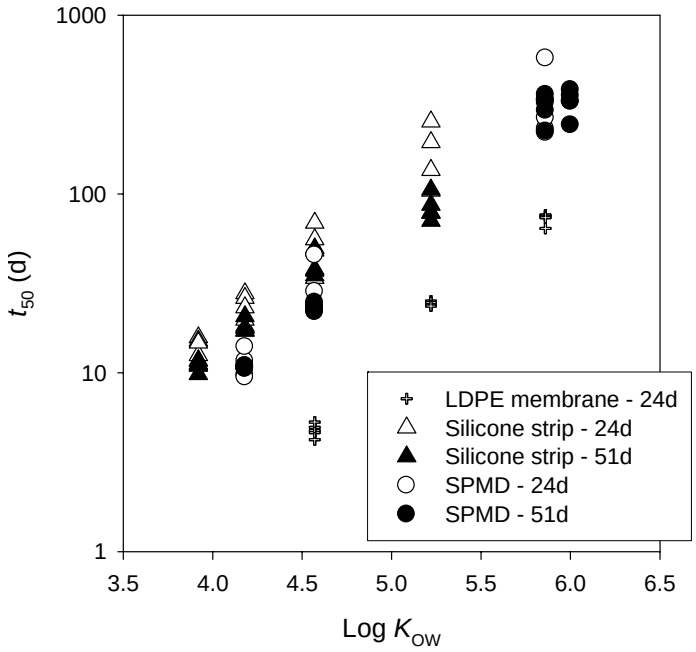

Figure 3-11. Time limit (days) for integrative sampling with these LDPE membranes, silicone strips and SPMDs.

Based on PRC elimination rates, $k_{e\text{-}PRC}$, it is possible to calculate equivalent uptake rates for non deuterated PRC analogues:

$$R_{S-PRC} = K_{SW} V_S k_{e-PRC}$$

where K_{SW} and V_S are the sampler-water partition coefficient and the volume of the sampler, respectively. Uptake rates for PRC analogues generally vary between 1.9 and 6.1 L d^{-1}.

Table 3-22. Equivalent uptake rates for PRC compounds (L d^{-1})

	R_S (L d^{-1})					
PRC	SPMD		Silicone strip		LDPE membrane	
	24 d	51 d	24 d	51 d	24 d	51 d
ACE-d_{10}	3.9 (*0.3*)	3.6 (*0.1*)	2.4 (*0.3*)	3.0 (*0.2*)	1.2 (*0.3*)	-
FLUE d_{10}	5.8 (*0.9*)	5.9 (*0.1*)	2.2 (*0.4*)	2.7 (*0.2*)	2.2 (*0.5*)	-
PHE d_{10}	5.3 (*1.3*)	6.1 (*0.3*)	1.9 (*0.5*)	2.3 (1.1)	4.5 (*0.4*)	-
FLUO-d_{10}	-	-	2.2 (*1.0*)	3.5 (0.6)	3.8 (*0.1*)	-
CHRY-d_{12}	3.3 (*1.1*)	3.1 (*0.6*)	-	-	4.6 (*1.8*)	-
B*e*P-d_{12}	-	3.3 (*0.6*)	-	-	-	-

3.4.1.1 PRC data vs. empirical R_S model for SPMDs

A model recently developed and published [14] was used to extrapolate uptake rates for the range of log K_{OW} 3.5-8 from PRC-based uptake rates. The application of the model as shown below slightly underestimates PRC-based uptake rates for log K_{OW} < 5 while it overestimates R_S for those at log K_{OW} ~ 6. In our case, elimination of PRC with log K_{OW} ~ 6 appeared significant while in many cases, only elimination rates for PRCs with log K_{OW} < 5 are available (Figure 3-12).

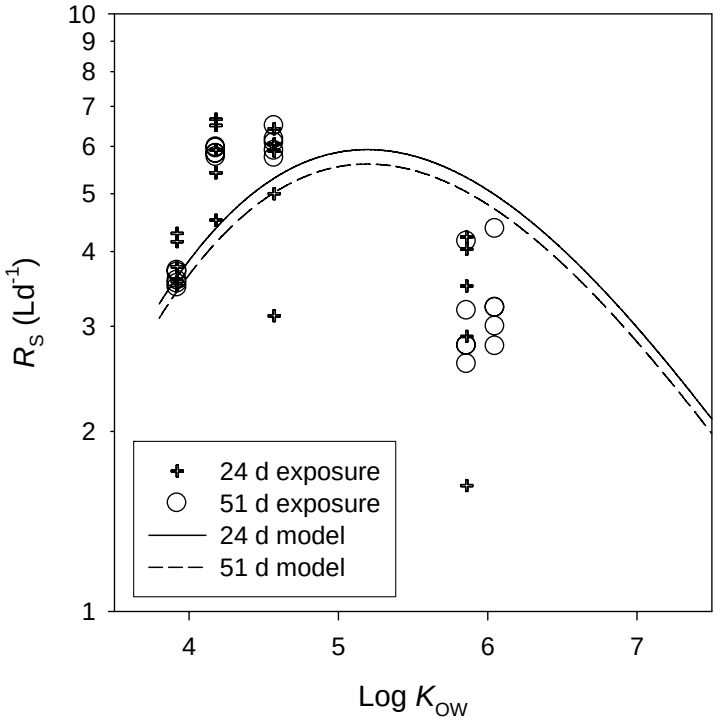

Figure 3-12. Comparison of PRC-derived uptake rates, R_S (L d^{-1}) for SPMD samplers with those estimated from the application of the model using PRC data.

3.4.2 Monitoring of PAHs and PBDEs with SPMD samplers

SPMD extracts were analysed for a suite of PAHs as shown in Table 3-23. Analytical limits of detection were close to 5 ng of each analyte per SPMD extract. Only residual levels of dibenzothiophene and phenanthrene were present in blanks. For phenanthrene these concentrations were negligible as they were < 10 % of the amount absorbed during 24 or 51 day exposures. Relative standard deviations on the masses absorbed were in the range 5-10 % in most cases. PAHs up to benzo[*e*]pyrene showed significant accumulation in the samplers, however concentrations of benzo[*a*]anthracene and other larger MW PAHs were below limits of detection, despite the relatively long exposure time of 51 days.

Table 3-23. Masses of PAHs absorbed into SPMD samplers (ng) after 24 and 51 day exposures in the Drammenselva River.

	Min. LOD (ng SPMD^{-1})	Mass absorbed (ng SPMD^{-1})

		Blanks[a]	24 day exposure[b]	51 day exposure[b]
ACY	5	<5	6.4 (*1.3*)*	10.7 (*1.3*)
ACE	5	<5	7.6 (*0.9*)	8.3 (*0.3*)
FLUE	5	<5	20.4 (*2.9*)	27.2 (*1.3*)
DBTHIO	5-16	<5-16	7.7 (*1.9*)	7.8 (*1.4*)
PHE	5	11.0 (*1.1*)	116 (*15*)	182 (*13*)
ANT	5	<5	6.3 (*0.8*)	10.1 (*1.1*)
FLUO	5	<5	46.8 (*3.3*)	114 (*5.5*)
PYR	5	<5	27.4 (*2.4*)	67 (1.6)
B*a*A	5	<5		
CHRY	5	<5	6.8 (*1.2*)	14.4 (*0.9*)
B*bj*F	5	<5		10.4 (*0.6*)
B*k*F	5	<5		
B*e*P	5	<5		6.8 (*0.3*)
B*a*P	5	<5		
PeR	5	<5		
In*123cd*P	5	<5		
DB*ah*A	5	<5		
B*ghi*P	5	<5		
[a]Mean of replicate values; [b]Mean of 5 replicate values; *Mean of 4 replicate (with 1 replicate <LOD);				

SPMD extracts were split into two fractions. The remaining fraction was analysed for brominated flame retardants. Many BDEs were below limits of detection for blanks, trip blanks and exposed samplers (Table 3-24). For most BDEs that were detected in exposed samplers, amounts in the blanks were not negligible (e.g. BDE47, BDE85, BDE99 and BDE100). Contamination may be present in the samplers prior to exposure or may be the result of absorption of these compounds from air during manipulation of the samplers. It generally appears that only the accumulation of BDE47 after 51 day exposure is significant.

Table 3-24. Masses of PBDEs absorbed into SPMD samplers (ng) after 24 and 51 day exposures in the Drammenselva River.

	Min. LOD (ng $SPMD^{-1}$)	Max. LOD (ng $SPMD^{-1}$)	Mass absorbed (ng $SPMD^{-1}$)		
			Blanks[a]	24 day exposure[b]	51 day exposure[b]
BDE28	0.03	0.05			
BDE47			**0.34 (*0.08*)**	**0.40 (*0.11*)**	**0.54 (*0.06*)**
BDE49	0.03	0.05			
BDE66	0.03	0.32			
BDE71	0.04	0.05			
BDE77	0.03	0.04			
BDE85	0.03	0.04	0.05 (*0.015*)	0.04*	0.06*
BDE99			0.27 (*0.11*)	0.32 (*0.11*)	0.40 (*0.16*)
BDE100	0.04		0.11 (*0.014*)	0.10 (*0.03*)	0.07 (*0.015*)
BDE119	0.04	0.07			
BDE138	0.1	0.14			
BDE153	0.04	0.07			

BDE154	0.03	0.1			
BDE183	0.03	0.03	0.50 (*0.09*)	0.43*	
BDE196	0.9	0.9			
BDE205	0.1	0.1			
BDE209	0.5	0.9			
[a]Mean of replicate values; [b]Mean of 5 replicate values; *only 1 value above LOD					

3.4.3 Monitoring of PAHs and PBDEs with silicone strip samplers

Since silicone strip samplers were weighed prior to extraction and analysis, it was possible to normalise the data to the weight of the sampler and its surface area (using density of silicone of 1.16 g cm^3). For comparison purposes, the data was then normalised to the nominal surface area of SPMD (i.e. 460 cm^2). Extracts were analysed for PAHs and detection limits for these silicone strip samplers were similar to those obtained with SPMD. This is not surprising since samplers had similar surface areas and were deployed in a similar way. Masses absorbed also appear to be in a similar range to those found in SPMDs (Table 3-25). PAHs with larger MW than benzo[*k*]fluoranthene were below limits of detection even for the 51 day exposure. Levels of acenaphthene, fluorene, dibenzothiophene and phenanthrene were above limits of detection for blanks with consistently slightly higher levels in trip blanks.

Table 3-25. Masses of PAHs absorbed into silicone strip samplers (ng) after 24 and 51 day exposures in the Drammenselva River.

	Min. LOD (ng sampler^{-1})	Mass absorbed (ng sampler^{-1})		
		Blanks & trip blanks[a]	24 day exposure[b]	51 day exposure[b]
ACY	5	<5	16.0 (*1.0*)	26.5 (*1.6*)
ACE	5	6.7 (*0.8*) 8.6 (2.2)	10.9 (*1.5*)	13.3 (*0.8*)
FLUE	5	11.7 (*2.3*) 16.2 (*6.1*)	38.1 (*4.4*)	52.9 (*2.9*)
DBTHIO	5-30	<5-30		22.8 (*5.3*)
PHE	5	26.9 (*6.7*) 33.3 (*14.9*)	154 (*23*)	320 (*45*)
ANT	5	<5	15.7 (*1.5*)	32.2 (*4.6*)
FLUO	5	<5 5.4*	44.9 (*6.3*)	114.9 (*2.9*)
PYR	5	<5	28.1 (*4.8*)	67.1 (*2.5*)
B*a*A	5	<5	6.0 (0.6)	11.3 (*2.0*)
CHRY	5	<5	7.0 (*1.6*)	16.3 (*1.2*)
B*bj*F	5	<5	5.3 (*0.7*)**	10.3 (*0.9*)
B*k*F	5	<5		6.7 (*0.4*)
B*e*P	5	<5		5.7 (*0.3*)
B*a*P	5	<5		
PeR	5	<5		
In*123cd*P	5	<5		
DB*ah*A	5	<5		
B*ghi*P	5	<5		
[a]Mean of replicate values; [b]Mean of 5 replicate values; *Only one value >LOD; **mean				

of two value >LOD
Blank values were subtracted when applicable (with standard deviation based on standard deviations of exposed samplers and those of blank samplers)

Analysis for polybrominated diphenyl ethers was conducted on extracts from silicone strip samplers. Interestingly, BDE levels in silicone strip were relatively high compared with those measured in SPMDs (Table 3-26). Most BDEs were above limits of detection in blank sampler. This certainly signifies that the different steps in sampler clean-up, preparation and extraction will need to be investigated in order to reduce these levels in blanks. BDEs present in the air during preparation of the samplers, may be readily absorbed by the samplers. In most cases, levels in exposed samplers were not significantly different from those in blank samplers and generally variable data was obtained. As for SPMD, only BDE47 appear to shown significant accumulation in the samplers during both the 24 and 51 day exposures. However it has to be noted that masses absorbed during the 51 day exposure exhibit relatively high variability.

Table 3-26. Masses of PBDEs absorbed into silicone strip samplers (ng) after 24 and 51 day exposures in the Drammenselva River.

	Min. LOD (ng sampler^{-1})	Max. LOD (ng sampler^{-1})	Mass absorbed (ng sampler^{-1})		
			Blanks[a]	24 day exposure[b]	51 day exposure[b]
BDE28	0.03	0.06	0.04 (*0.01*)*	0.05*	
BDE47			**0.17 (*0.16*)**	**0.40 (*0.03*)**	**1.17 (*0.62*)**
BDE49	0.1	0.14	0.10 (*0.06*)	0.15 (*0.02*)*	0.18 (*0.01*)*
BDE66			0.10 (*0.05*)	0.11 (0.02)	0.14 (*0.02*)
BDE71	0.04	0.12	0.08 (*0.04*)*		0.10*
BDE77	0.03	0.1	0.06 (*0.01*)*	0.05*	
BDE85			0.21 (*0.16*)	0.17 (*0.05*)	0.24 (*0.08*)
BDE99			0.98 (*1.74*)	0.34 (*0.06*)	1.28 (*1.1*)
BDE100			0.40 (*0.25*)	0.35 (*0.08*)	0.52 (*0.11*)
BDE119			0.29 (*0.10*)	0.36 (*0.07*)	0.35 (*0.11*)
BDE138	0.2	0.4			
BDE153	0.04	0.07	0.83*		0.38 (*0.16*)*
BDE154			0.38 (*0.23*)	0.28 (*0.08*)	0.38 (*0.12*)
BDE183			2.12 (*0.60*)	1.93 (*0.34*)	1.83 (*0.41*)
BDE196			3.26 (*0.36*)	2.85 (*0.64*)	2.53 (*0.48*)
BDE205			0.24 (*0.02*)	0.20*	
BDE209	0.04	4			

[a]Mean of replicate values; [b]Mean of 5 replicate values; *less than 4 values > LOD
2 samplers were obvious outliers with masses measured at > 100x all other values

3.4.4 Monitoring of PAHs and PBDEs with LDPE membrane samplers

For operational reasons, these samplers were only deployed for the 24 day period. Since LDPE membrane samplers were weighed prior to extraction and analysis, it was possible to normalise the data to the weight of the sampler and its surface area (using density of LDPE of 0.91 g cm^3). For comparison purposes, the data was then normalised to the nominal surface area of SPMD (i.e. 460 cm^2). Analysis for PAHs revealed that levels of acenaphthylene,

fluorene, phenanthrene and chrysene were above limits of detection in blanks and trip blank samplers (Table 3-27). Levels of acenaphthylene and fluorene were lower in exposed samplers compared with blanks and trip blanks. Bearing in mind the time limit for integrative sampling provided in the previous section, concentration of these analytes in the LDPE membrane samplers were close to equilibrium with the concentration in water. So it is very likely that these analytes were lost from the samplers during "re-equilibration". Pyrene and fluoranthene were the largest MW PAHs detected by these samplers during the 24 day exposure.

Table 3-27. Masses of PAHs absorbed into LDPE membrane samplers (ng) after a 24 day exposure in the Drammenselva River.

	Min. LOD (ng sampler^{-1})	Mass absorbed (ng sampler^{-1})	
		Blanks & trip blanks[a]	24 day exposure[b]
ACY	5	39.2 (*2.5*) 39.7 (*0.8*)	7.0 (*0.9*)
ACE	5	<	<
FLUE	5	18.2 (*2.0*) 18.7 (*0.9*)	8.3 (*0.7*)
DBTHIO	5	<	<
PHE	5	14.9 (*2.2*) 13.0 (0.7)	48.1 (*2.1*)
ANT	5	<	<
FLUO	5	<	33.3 (*1.3*)
PYR	5	<	25.2 (*0.7*)
B*a*A	5	<	<
CHRY	5	7.5 (*1.7*)* 9.8 (*0.6*)*	<
B*bj*F	5	<	<
B*k*F	5	<	<
B*e*P	5	<	<
B*a*P	5	<	<
PeR	5	<	<
In*123cd*P	5	<	<
DB*ah*A	5	<	<
B*ghi*P	5	<	<

[a]Mean of replicate values; [b]Mean of 5 replicate values
*this is unexpected and cannot be explained

Extracts from LDPE membrane samplers were also analysed for brominated flame retardants. Most BDEs were below limits of detection for blanks, trip blanks as well as exposed samplers (Table 3-28). BDE47 and BDE99 were the only BDEs detected in LDPE membrane samplers following a 24 day exposure. For BDE99, three samplers out of five were above limits of detection.

Table 3-28. Masses of PBDEs absorbed into LDPE membrane samplers (ng) after a 24 day exposure in the Drammenselva River.

	Min. LOD	Max. LOD	Mass absorbed (ng sampler^{-1})

	(ng sampler^{-1})	(ng sampler^{-1})		
			Blanks[a]	24 day exposure[b]
BDE28	0.1		<0.1	
BDE47	0.07		<0.07	0.175 (*0.036*)
BDE49	0.04	0.06	<0.04	
BDE66	0.03	0.05	<0.03	
BDE71	0.04	0.06	<0.04	
BDE77	0.05	0.06	<0.05	
BDE85	0.03	0.05	<0.03	
BDE99	0.06	0.13*	<0.06	0.127 (*0.012*)**
BDE100	0.05		<0.05	
BDE119	0.06		<0.06	
BDE138	0.08	0.09	<0.08	
BDE153	0.05	0.07	<0.05	
BDE154	0.04	0.05	<0.04	
BDE183	0.12		<0.12	
BDE196	0.6		<0.6	
BDE205	0.13		<0.13	
BDE209	0.5	2.1	<0.5	
[a]Mean of replicate values; [b]Mean of 5 replicate values; *1 sample with high LOD; **3 values were measurably above LOD out of the 5 exposed samplers				

3.4.5 Integrative monitoring

Integrative monitoring may be achieved by keeping the sampler exposure duration well below the time needed for the analyte concentration in the sampler to reach equilibrium with that in the water. Performance reference compound data (see previous section) demonstrated that for analyte with log $K_{OW} > 5$, uptake remained linear during both the 24 and 51 day exposures. Since all passive sampling devices were produced with the same configuration (2.5 cm wide and 92 cm long) irrespectively of the type of material used, we can expect that for analytes under boundary layer controlled uptake ($R_S = AD_W/\delta_W$), the material samplers are made of does not influence the accumulation rate (that is when the capacity of the sampler is sufficiently high).

Masses of pyrene, fluoranthene and chrysene absorbed by the different samplers over the 24 day exposure were very similar (Figure 3-13). Slightly lower values for LDPE membrane samplers could be the result of the samplers being slightly smaller than expected, or it may be that these samplers were not in the linear phase of uptake anymore and the accumulated rate reduced (see PRC data). The 51 day exposure allowed the quantification of more PAHs than the 24 day exposure (Figure 3-14). The 51 day exposure of silicone strips and SPMDs resulted in extremely similar masses of analytes absorbed.

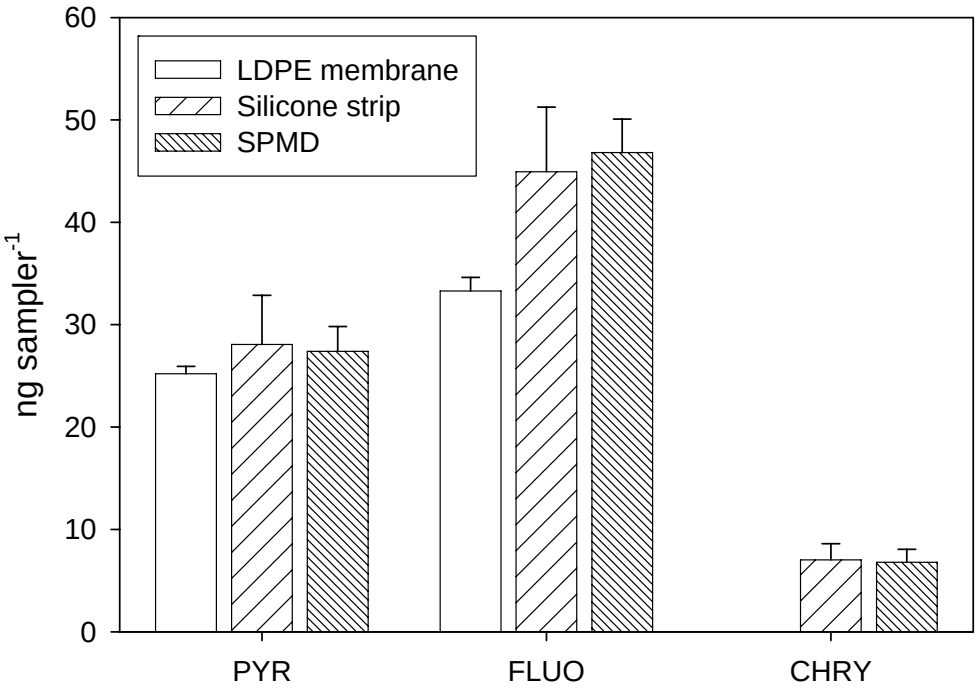

Figure 3-13. Masses of pyrene (PYR), fluoranthene (FLUO) and chrysene (CHRY) absorbed in the different passive sampling devices following a 24 day exposure in the Drammenselva River. Linear/integrative sampling is expected for these compounds. The generally very similar masses accumulated indicate that these compounds are under boundary layer controlled uptake.

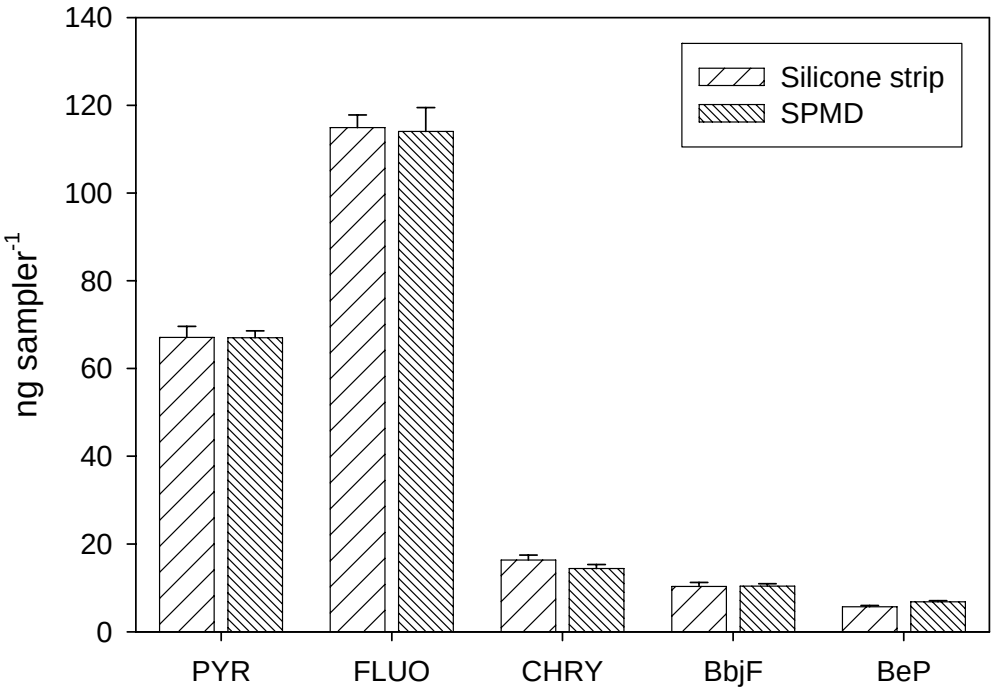

Figure 3-14. Masses of pyrene (PYR), fluoranthene (FLUO), chrysene (CHRY), benzo[b,j]fluoranthene (BbjF) and benzo[e]pyrene (BeP) absorbed in the different passive sampling devices following a 51 day exposure in the Drammenselva River. Linear/integrative sampling is expected for these compounds. The generally very similar masses accumulated indicate that these compounds are under boundary layer controlled uptake. Note: LDPE membranes were not exposed for 51 days.

If (i) water temperature, (ii) turbulences around the samplers and (iii) contaminant concentrations were identical for the two exposure periods, masses of analyte absorbed by the samplers exposed for 51 days should be higher than those in samplers exposed for 24 days by a factor of 51/24. Ratios of contaminant masses absorbed by silicone strips and SPMD normalised to respective exposure times ((m_{51d}/51)/(m_{24d}/24)) were plotted to identify the range of analytes for which sampling was integrative and those that were closer to equilibrium (Figure 3-15). A ratio of 1 indicates that sampling over the 51 days was integrative, while a ratio of 0.47 signifies that equilibrium was reached after 24 days. For the silicone strips, it appears that the threshold for integrative sampling was for analytes with log K_{OW} between 4.5 and 5 (see figure below). Data from both types of samplers generally appear consistent, however difference may be observed for phenanthrene and anthracene for which ratio are close to 0.8 for SPMD and just below 1.0 for silicone strips.

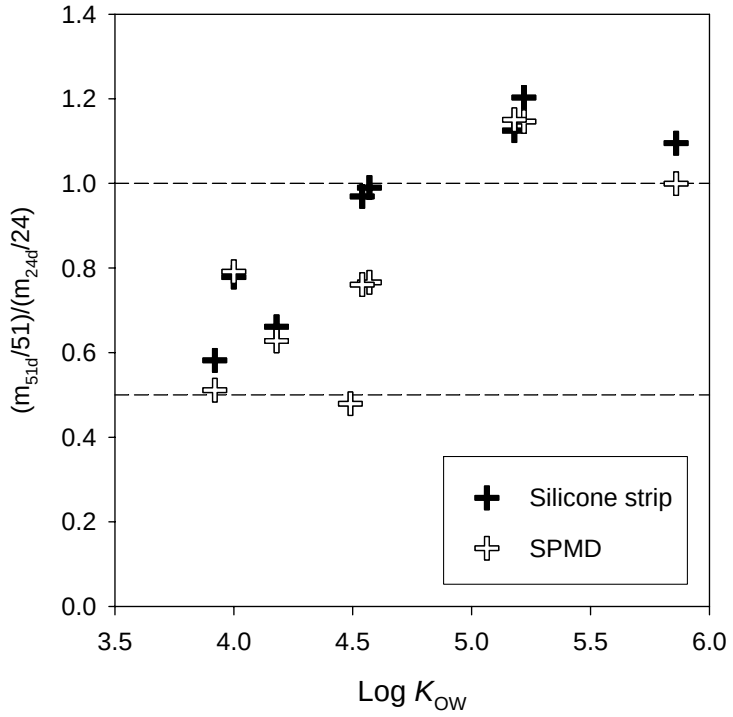

Figure 3-15. Ratios of masses of analytes accumulated over 51 and 24 day exposures normalised to respective exposure durations. Ratios of 1 are expected if sampling is (i) integrative, (ii) if no changes in water turbulences near the samplers occur during the two exposures and (iii) if the dissolved PAH concentration in water does not vary significantly during the 51 day period. A ratio of 0.5 should be observed if equilibrium is reached within 24 days.

3.4.6 Time-weighted average concentrations (C_{TWA})

Time-weighted average (TWA) concentrations can be calculated in a number of different ways. However, the use of performance reference compound data provides a more reliable estimation of in situ uptake rates than the use of laboratory-based uptake rate values. Uptake rates for PRC analogues may be estimated from elimination rates (k_e):

$$R_{S-PRC} = K_{SW} V_S k_e$$

Once the R_S value is known, it is possible to calculate the TWA concentration from the contaminant mass absorbed:

$$C_{TWA} = \frac{m}{K_{SW} V_S (1 - e^{-\frac{R_S}{K_{SW} V_S} t})}$$

This equation accounts for situations where the uptake is not linear anymore (when approaching equilibrium). When at equilibrium this simplifies to:

$$C_{TWA} = \frac{m}{K_{SW} V_S}$$

However when uptake is linear, the equation transforms to:

$$C_{TWA} = \frac{m}{R_S t}$$

For the remaining part of this report, TWA concentrations are calculated using the full equation so as to minimise possibilities of errors.

As shown by these equations, an accurate determination (or availability of accurate values) of analyte sampler-water partition coefficients is crucial to an accurate estimation of R_S values. The estimation of these values relies on the K_{SW} and the elimination rates observed for performance reference compounds [6].

More details of the estimation of TWA concentrations for SPMDs, LDPE membranes and silicone strips are provided below.

3.4.6.1 SPMDs

For SPMDs, an empirical model based on log K_{OW} was published [14] and allows the estimation of R_S values from PRC elimination rates and compounds log K_{OW}. This model is based on extensive laboratory-based calibration data and predicts a strong decrease in uptake rates with increasing log K_{OW} for analytes under boundary layer controlled uptake. This decrease appears much strong than that predicted if the reduction in diffusion coefficients with increasing analyte molecular weight (MW) was solely responsible for the decrease. It is important to state this here, as the use of this model would be expected to provide different uptake rate values (and TWA concentrations) to those estimated for LDPE membranes and silicone strips since such model is not available for these samplers. Estimation of uptake rates for SPMDs is therefore conducted using the published model. TWA concentration for PAHs are provided in Table 3-29 and shown graphically on Figure 3-16. Those for PBDEs are given in Table 3-30.

Table 3-29. Time-weighted average concentration of dissolved PAHs in the Drammenselva measured using SPMDs exposed for 24 and 51 days. The published R_S-log K_{OW} model was used to determine uptake rates.

	C_{TWA} (pg L^{-1})	
	24 day exposure[a]	51 day exposure[a]
ACY	135 (*24*)*	186 (*21*)
ACE	186 (*18*)	172 (*5*)
FLUE	331 (*67*)	332 (*17*)
DBTHIO	89 (*11*)	59 (*11*)
PHE	1123 (*251*)	1170 (*94*)
ANT	68 (*13*)	72 (*8*)
FLUO	370 (*15*)	498 (*18*)
PYR	217 (*5*)	297 (*11*)
B*a*A	< 42	30 (*4*)
CHRY	56 (*11*)	62 (*6*)
B*bj*F	<42	45 (*2*)
B*k*F	<42	<22
B*e*P	<44	31 (*1*)
B*a*P	<44	<22
PeR	<47	<24
In*123cd*P	<53	<27
DB*ah*A	<61	<31
B*ghi*P	<53	<27
[a]Mean of 5 replicate values; *Mean of 4 replicate (with 1 replicate <LOD);		

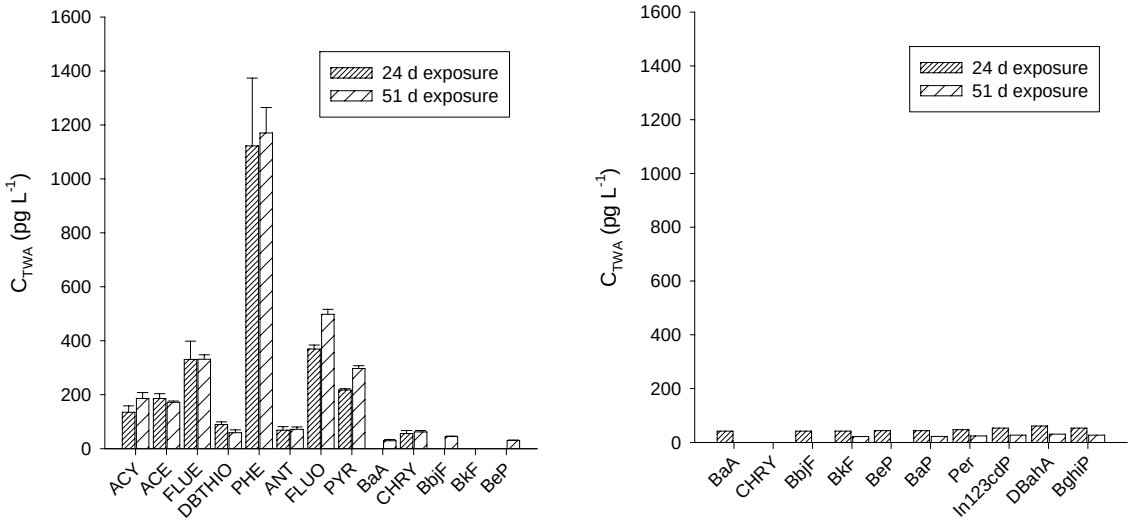

Figure 3-16. Dissolved PAH concentrations (left) measured with SPMDs exposed for 24 and 51 days and limits of detection for those that were below limits of detection (right).

Table 3-30. Time-weighted average concentration of dissolved PBDEs in the Drammenselva measured using SPMDs exposed for 24 and 51 days. The published empirical R_S-log K_{OW} model was used to determine uptake rates.

	C_{TWA} (pg L^{-1})	
	24 day exposure[a]	51 day exposure[a]
BDE28	<0.3-0.5	<0.2-0.3
BDE47	**0.68**	**1.16**
BDE49	<0.4-0.6	<0.2-0.3
BDE66	<0.4-3.6	<0.17-1.8
BDE71	<0.5-0.6	<0.3-0.4
BDE77	<0.4-0.5	<0.2-0.3
BDE85	0.5-0.7	0.3-0.4
BDE99	16*	8*
BDE100	<0.7	<0.4
BDE119	<0.7-1.2	<0.4-0.6
BDE138	<2.6-3.6	<1.3-1.8
BDE153	<1.1-1.8	<0.5-0.9
BDE154	<0.8-2.6	<0.4-1.3
BDE183	<1.3	<0.7
BDE196	<60	<30
BDE205	<10	<5.1
BDE209	<69-124**	<37-66**
[a]Mean of 5 replicate values; *LOQ calculated as 3x the		

mean of blank values **High LODs and applicability of the SPMD model to such hydrophobic molecule is disputable

3.4.6.2 LDPE membranes

A different strategy is needed to estimate uptake rates for LDPE membrane and silicone strip sampler since no empirical R_S-log K_{OW} relationships are available for these sampling devices. The uptake rate is related to the overall mass transfer coefficient k_O:

$$R_S = Ak_O = \frac{A}{\frac{1}{k_W} + \frac{1}{K_{SW}k_m}} = \frac{A}{\frac{\delta_W}{D_W} + \frac{\delta_m}{K_{SW}D_M}}$$

When uptake is under boundary-layer control, this equation reduces to:

$$R_S = \frac{AD_W}{\delta_W}$$

From [6], the molecular diffusion coefficient D_W for PAHs (at 13 °C) can be related to log K_{OW}:

$$\log D_W = -8.96 - 0.0659 \log K_{OW} \quad R = 0.94, s = 0.02, n = 17$$

Considering that $k_W \sim D_W^{2/3}$, the boundary layer mass transfer coefficient can be re-written as:

$$k_W = B_W K_{OW}^{-0.044}$$

Since some performance reference compounds have been shown to be under water boundary layer controlled uptake these can be used to estimate the B_W parameter. For LDPE membranes and silicone strips, this enables the estimation of R_S values for analytes under boundary layer controlled uptake. For analytes under membrane controlled uptake, analyte diffusion coefficients for the polymer material, D_M, and sampler-water partition coefficients, K_{SW}, may be used to estimate the contribution of mass transfer resistance in the membrane [19, 20]. This can also be applied to PRCs under boundary layer controlled offload. The mass transfer coefficient for the boundary layer, k_W may be estimated from the elimination rate and with knowledge of K_{OW}, B_W can be calculated. For LDPE membrane samplers, the 24 day exposure resulted in a value of 1.83 μm s^{-1} with a relative standard deviation of 26 % (Table 3-31). This value is significantly lower than those obtained by [6], however water turbulences and velocity near the samplers were significantly higher than in the present deployment. This is illustrated by the significantly higher uptake rates they observed. This parameter allows the estimation of uptake rates for all analytes (PAHs and PCBs) under boundary layer controlled uptake.

Table 3-31. Values of parameter B_W for LDPE exposures estimated from PRC data under boundary layer controlled uptake.

	LDPE membrane exposure	
	24 days	51 days
B_W (μm s^{-1})	1.83 (*0.49*)	-

Calculated limits of detections with respect to dissolved phase concentrations were below 0.06 ng L^{-1} for most PAHs. Higher LODs were observed for acenaphthalene, dibenzothiophene and anthracene. This is because the uptake for these compounds was close to reaching equilibrium and the small volume of the sampler relative to the other samplers was responsible for low masses absorbed. The C_{TWA} measured for phenanthrene was very close to the values measured with SPMDs (Table 3-32). Concentrations measured for

fluoranthene and pyrene (0.47 and 0.37 ng L^{-1}, respectively) are slightly higher than those found with SPMDs (0.37 and 0.22 ng L^{-1}, respectively for the 24 day exposure). The 51 day exposure of SPMDs resulted in measured concentrations for these compounds that are closer to values found for LDPE membranes (Figure 3.17).

Table 3-32. Time-weighted average concentration of dissolved PAHs in the Drammenselva measured using LDPE membranes exposed for 24 and 51 days.

	C_{TWA} (pg L^{-1})
	24 day exposure[a]
ACY	*
ACE	<710
FLUE	*
DBTHIO	<250
PHE	1171 (*55*)
ANT	<180
FLUO	470 (*32*)
PYR	370 (*31*)
B*a*A	<57
CHRY	<57
B*bj*F	<57
B*k*F	<57
B*e*P	<57
B*a*P	<57
PeR	<57
In*123cd*P	<57
DB*ah*A	<58
B*ghi*P	<57
[a]Mean of 5 replicate values; *PAH detected in blank samplers	

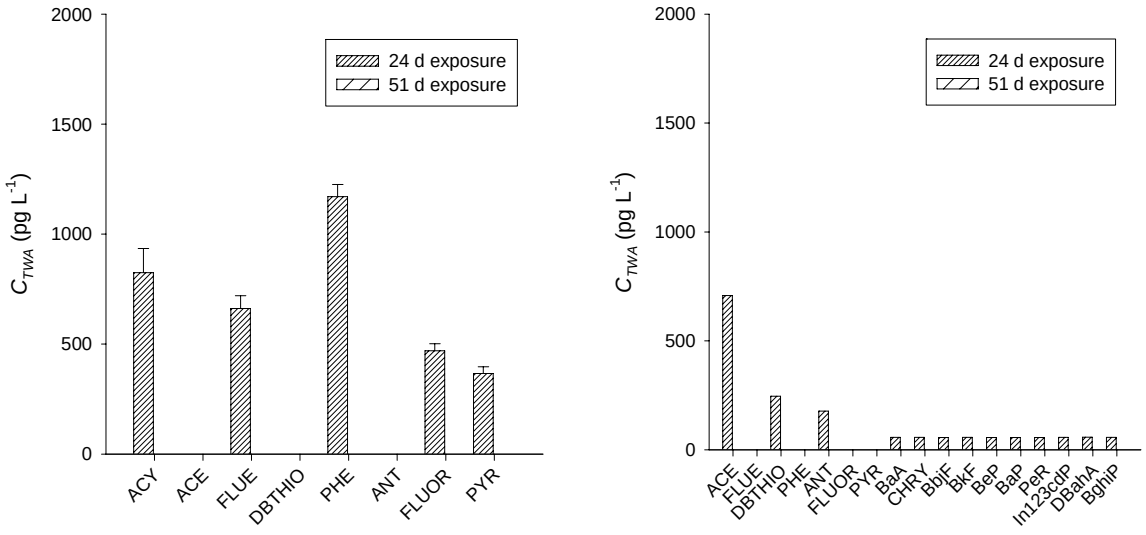

Figure 3-17. Dissolved PAH concentrations (left) measured with LDPE membrane samplers exposed for 24 and 51 days and limits of detection for those that were below limits of detection (right).

The situation for PBDEs is complicated since significant uncertainty is associated with many of the parameters involved here [65, 66]. These also include diffusion coefficients for these analytes in the polymer and in water as well as sampler-water partition coefficients. However, to estimate sampling rates, we can assumed that the membrane does not become the rate limiting step in the uptake of PBDEs from water, rather we assumed that the transfer across the boundary layer still controls the uptake. In this case:

$$D_W \sim MW^{-0.53}$$

And

$$k_W \sim D_W^{2/3}$$

So that:

$$k_W \sim MW^{-0.35}$$

Since *MW* for PBDEs are known, we can estimate the thickness of the boundary layer and D_W and therefore R_S. As shown previously most PBDEs were below limits of detection. Uptake rates calculated here allowed estimating limits of detection in terms of dissolved concentrations in water based on analytical limits of detection. These values vary in the range 0.4 to 35 pg L^{-1} (Table 3-33). A dissolved concentration of 1.3 pg L^{-1} for BDE47 was found while an estimate for that of BDE99 was 0.9 pg L^{-1}.

Table 3-33. Time-weighted average concentration of dissolved PBDEs in the Drammenselva measured using LDPE membranes exposed for 24 and 51 days.

	C_{TWA} (pg L^{-1})
	24 day exposure[a]
BDE28	<1.2
BDE47	**1.3 (*0.5*)***
BDE49	<0.5-0.8
BDE66	<0.4-0.6

BDE71	<0.5-0.8
BDE77	<0.6-0.8
BDE85	<0.4-0.7
BDE99	**0.9*,****
BDE100	<0.7
BDE119	<0.8
BDE138	<1.1-1.3
BDE153	<0.7-1.0
BDE154	<0.6-0.7
BDE183	<1.8
BDE196	<9.2
BDE205	<2.1
BDE209	<8.2-35
[a]Mean of 5 replicate values; *The LOD of blank samplers was subtracted from the mass accumulated to calculate C_{TWA}; ** only three values > LOD	

3.4.6.3 Silicone strips

A similar procedure to that used for LDPE membranes was used to determine uptake rates for PAHs and PBDEs by silicone strips. The parameter B_W was estimated based on PRC data under boundary controlled mass transfer for both exposures (Table 3-34). Values approximately half of the one obtained for LDPE membrane samplers were calculated.

Table 3-34. Values of parameter B_W for silicone strip exposures of 24 and 51 days estimated from PRC data under boundary layer controlled uptake.

	Silicone membrane exposure	
	24 days	51 days
B_W (μm s^{-1})	0.85 (*0.28*)	1.16 (*0.27*)

Most analytes were expected to be under boundary layer controlled uptake and the model used for LDPE using the empirical parameter B_W described above was applied to the silicone strips data. Dissolved PAH concentrations measured with silicone strip samplers were significantly higher than those measured with SPMD or LDPE membrane samplers (Table 3-35 and Figure 3-18). On average, concentrations were a factor of 2 to 10 above those measured by SPMD and calculated using the model by [14].

Table 3-35. Time-weighted average concentration of dissolved PAHs in the Drammenselva measured using silicone strips exposed for 24 and 51 days.

	C_{TWA} (pg L^{-1})	
	24 day exposure[a]	51 day exposure[a]
ACY	830 (*40*)	1265 (*75*)
ACE	315 (*50*)	273 (*6*)
FLUE	990 (*190*)	819 (*33*)
DBTHIO	<450	227 (*82*)
PHE	3531 (*720*)	3427 (*460*)
ANT	352 (*53*)	318 (*45*)

FLUO	990 (*130*)	969 (*52*)
PYR	610 (*75*)	554 (*39*)
B*a*A	135 (*20*)	92 (*16*)
CHRY	156 (*17*)	132 (*13*)
B*bj*F	116 (*18*)	82 (*11*)
B*k*F	<114	53 (*3*)
B*e*P	<116	46 (*3*)
B*a*P	<116	<40
PeR	<118	<41
In*123cd*P	<121	<42
DB*ah*A	<124	<43
B*ghi*P	<121	<42
[a]Mean of 5 replicate values; *Mean of 4 replicate (with 1 replicate <LOD);		

For PBDEs, levels in blank or control samplers were above levels of detection and further clean-up or improvement in manipulation of the samplers may be needed to reduce background levels and improve the usability of the sampler. BDE47 was the only analyte for which increases in mass absorbed with increasing exposure time were observed. This resulted in the estimation of dissolved BDE47 concentrations of 6.1 and 9.3 pg L^{-1} for exposures of 24 and 51 days, respectively (Table 3-36). Limits of detection are in the range 0.8-63 and 0.3 to 48 pg L^{-1} in the dissolved phase for exposures of 24 and 51 days, respectively.

Table 3-36. Time-weighted average concentration of dissolved PBDEs in the Drammenselva measured using silicone strips exposed for 24 and 51 days.

	C_{TWA} (pg L^{-1})	
	24 day exposure[a]	51 day exposure[a]
BDE28	<0.8-1.5	<0.3-0.6
BDE47	**6.1***	**9.3***
BDE49	<1.7-2.6	<0.9-1.4
BDE66	*	*
BDE71	<1.1-1.5	<0.4-1.2
BDE77	<0.8-1.2	<0.3-0.9
BDE85	*	*
BDE99	*	*
BDE100	*	*
BDE119	*	*
BDE138	<5.5-5.8	<2.1-4.2
BDE153	<1.0-1.2	<0.4-0.7
BDE154	*	*
BDE183	*	*
BDE196	*	*
BDE205	*	*
BDE209	<1.3-63	<0.5-48
[a]Mean of 5 replicate values; *relatively high blank levels		

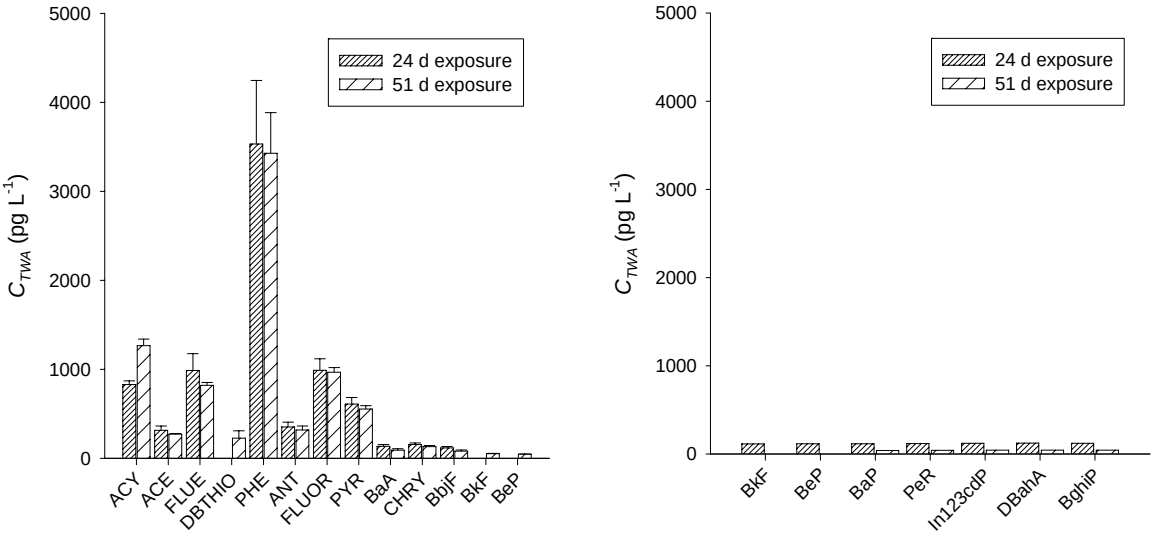

Figure 3-18. Dissolved PAH concentrations (left) measured with silicone strips exposed for 24 and 51 days and limits of detection for those that were below limits of detection (right).

3.4.7 Monitoring of PCBs and TBT with SPMD devices

Two successive SPMD exposures were undertaken in the Drammenselva River during this field test. Following exposure samplers were extracted and analysed for a range of PCBs and organochlorines and for organotin species (Tables 3-37 and 3-38). All of the PCBs were below limits of detection at the 1 ng $SPMD^{-1}$ level. Pentachlorobenzene, *p,p'*-DDE, *p,p'*-DDD as well as α- and γ-HCH were below limits of detection. Only hexachlorobenzene was detected in exposed samplers. Concentrations measured here were very close to those measured in the filtered fraction using the large volume water sampler. No CB28 or CB52 were detected in these samplers.

Table 3-37. Masses of PCBs and organochlorines absorbed by SPMD samplers deployed for 2 consecutive periods in the Drammenselva River.

	Concentration in SPMD (ng $SPMD^{-1}$)		
Analyte ID	Blank	1st exposure[a]	2nd exposure[a]
CB28	<1	<1	<1
CB52	<1	<1	<1
CB101	<1	<1	<1
CB118	<1	<1	<1
CB105	<1	<1	<1
CB153	<1	<1	<1
CB138	<1	<1	<1
CB156	<1	<1	<1
CB180	<1	<1	<1
CB209	<1	<1	<1
PeCB	<0,5	<0,5	<0,5

α-HCH	<1	<1	<1
HCB	<0,5	6.5 (*3.1*)*	2.3 (*0.1*)
γ-HCH	*i*	*i*	*I*
p,p'-DDE	<1	<1	<1
p,p'-DDD	<2	<2	<2
i: interferences on the chromatogram *1 values appears significantly higher than the two other replicates and may be an outlier [a]Mean value of triplicate measurements with SPMDs			

Table 3-38. Time-weighted average dissolved concentrations of organochlorines and PCBs measured with SPMD deployed for two consecutive periods of 28 and 23 days, respectively. Mean uptake rates from the other SPMD deployments were used for the calculation since these SPMDs were deployed in a similar manner to the others.

	C_{TWA} (pg L^{1})	
Analyte ID	1st exposure[a]	2nd exposure[a]
CB28	<7	<8
CB52	<7	<9
CB101	<9	<11
CB118	<11	<13
CB105	<10	<12
CB153	<12	<14
CB138	<11	<14
CB156	<14	<17
CB180	<16	<19
CB209	<32	<38
PeCB	<4	<4
α-HCH	<29	<31
HCB	**45 (*21*)***	**19 (*1*)**
γ-HCH	*i*	*I*
p,p'-DDE	<7	<8
p,p'-DDD	<15	<18
i: interferences on the chromatogram *1 values appears significantly higher than the two other replicates and may be an outlier; if removed, C_{TWA} = 32 (*2*) pg L^{-1} [a]Mean value of triplicate measurements with SPMDs		

Extracts were also screened for a series of organotins. It is not surprising not to detect any MBT since this sampler is not expected to accumulate any significant amounts of these compounds. All other compounds were below limits of detection. Based on log K_{OW} values for organotin in the range 3.2 to just > 4 and uptake rates similar to those used above, limits of detection for these compounds are in the range 20-100 pg L^{-1}.

Table 3-39. Masses of organotins absorbed by SPMD sampler deployed for 2 consecutive periods in the Drammenselva River.

	$C_{Sampler}$ (ng SPMD[1])	
Analyte ID	1st exposure[a]	2nd exposure[a]
MBT	<1	<1 (3.7*)
DBT	<1	<1
TBT	<1	<1
MPhT	<1	<1
DPhT	<1	<1
TPhT	<1	<1
*One value at 3.7 [a]Mean value of triplicate measurements with SPMDs		

3.4.8 Monitoring of PAHs and PBDEs in the Alna River with LDPE membrane and silicone strips

Following exposure, LDPE membrane and silicone strip samplers were extracted with pentane instead of methanol and this may have contributed to the slightly lower PBDE levels in the trip blanks for silicone strips. Only BDE99, BDE100, BDE154, BDE183 and BDE196 were above LOD in the blanks. All values for the trip control/blank of LDPE membrane samplers were below limits of detection. Significant accumulation of BDE28 and BDE 47 was observed both in LDPE membranes and silicone strips. Accumulation of BDE99 and BDE154 also appeared significant in LDPE membranes and BDE66 and BDE71 were detected in one extract (Table 3-40).

This is very promising since the water temperature (affecting diffusion in water) was very low and samplers were covered with ice for the final week or two of exposure. So it could be expected that under more commonly found situations and longer exposure, even more significant accumulation of these compounds is possible. PRC data is presently not available (awaiting analysis) and therefore, estimation of uptake rates and resulting time-weighted average concentrations without these would be unreliable.

Table 3-40. Mass of PBDEs (ng) absorbed by LDPE membrane and silicone strip samplers during exposure in the Alna River (Oslo). Samplers were deployed for 1 month from December 2008 until January 2009.

	PBDE mass absorbed (ng)							
	LDPE membrane				Silicone strip			
	Blanks	Trip blank	Replicate 1	Replicate 2	Blanks	Trip blank	Replicate 1	Replicate 2
BDE28	<0.1	<0.04	**0.15**	**0.17**	0.04 (*0.01*)	<0.05	**0.17**	**0.15**
BDE47	<0.07	<0.04	**1.15**	**1.28**	0.17 (*0.16*)	<0.05	**0.48**	**0.97**
BDE49	<0.04	<0.05	**0.10**	**0.10**	0.10 (*0.06*)	<0.06	<0.06	<0.14
BDE66	<0.03	<0.05	<0.07	**0.06**	0.10 (*0.05*)	<0.08	<0.04	<0.04
BDE71	<0.04	<0.04	<0.09	**0.09**	0.08 (*0.04*)	<0.09	<0.07	<0.17
BDE77	<0.05	<0.04	<0.05	<0.05	0.06 (*0.01*)	<0.05	<0.03	<0.04
BDE85	<0.03	<0.03	<0.08	<0.04	0.21	<0.1	<0.03	<0.03

					(*0.16*)			
BDE99	<0.06	<0.03	**0.57**	**0.58**	0.98 (*1.74*)	**0.13**	**0.26**	**0.41**
BDE100	<0.05	<0.04	<0.09	<0.08	0.40 (*0.25*)	0.20	0.05	0.09
BDE119	<0.06	<0.06	<0.09	<0.08	0.29 (*0.10*)	<0.1	<0.05	<0.09
BDE138	<0.08	<0.06	<0.07	<0.08		<0.2	<0.06	<0.07
BDE153	<0.05	<0.04	<0.04	<0.04	0.83	<0.08	<0.07	<0.07
BDE154	<0.04	<0.04	**0.11**	**0.06**	0.38 (*0.23*)	0.11	<0.03	<0.06
BDE183	<0.12	0.21	0.35	0.15	2.12 (*0.60*)	0.76	0.17	0.28
BDE196	<0.6	0.35	0.41	0.18	3.26 (*0.36*)	0.39	0.44	0.20
BDE205	<0.13	<0.11	<0.13	<0.09	0.24 (*0.02*)	<0.15	<0.05	<0.06
BDE209	<0.5	<0.2	<0.3	<0.4	0.04 (*0.01*)	<1.1	<0.8	<0.7

3.5 Screening of extracts for hexabromocyclododecane

Screening was undertaken for filter samples, centrifuge and SPM sampler extracts and the passive sampler extracts from the deployments in the Drammenselva and Alna Rivers. Results that were above limits of detection (1 ng per extract) are provided in Tables 3-41 and 3-42.

Table 3-41. Concentrations of HBCD diastereoisomers in 2 filter samplers from the large volume water sampler (ng Filter^{-1}).

	α-HBCD	β-HBCD	γ-HBCD
Filter 3	1.3	2	1.5
Filter 4	1	1	7
Blank	nd	nd	nd
Results are semi quantitative due to not having any internal standard and of the uncertainty of the exact volume of the extract.			

Due to the semi-quantitative nature of these results it is not possible to calculate concentrations in water; however it is likely that particulate phase concentrations of HBCD diastereoisomers were below 10 pg L^{-1}.

The silicone strip and LDPE membrane sampler data in Table 3-42 is very interesting. γ and α diastereoisomers of HBCD were apparently detected in silicone strips but not in LDPE membrane samplers. No HBCD was detected in either blank sampler. It is slightly surprising to detect HBCD with one type of sampler and not the other. There are two possibilities to explain this. Samplers had exactly the same surface area, but volumes of silicone strips are one order of magnitude larger than LDPE membranes'. If sampling had reached some form of equilibrium, then the smaller volume of LDPE may have resulted in masses absorbed below LOD. The second possibility is based on the fact that HBCD is a large molecule that may not be able to diffuse in the LDPE (or diffuse only very slowly). Uptake rates may therefore be

controlled by transport in the membrane rather than in boundary layer. Diffusion coefficients for such compounds are likely to be orders of magnitude higher in silicone than in LDPE [19, 20].

Table 3-42. Concentrations of HBCD isomers in passive sampler extracts (LDPE membranes and silicone strips) exposed in the Alna river for 1 month (ng extract^{-1}).

	α-HBCD	β-HBCD	γ-HBCD
Silicone strip Rep-1	3.5	nd	2.5
Silicone strip Rep-2	2.5	nd	1.8
Silicone strip Blank	nd	nd	nd
LDPE Membrane Rep-1	2	nd	nd
LDPE Membrane Rep-2	nd	nd	nd
LDPE Membrane Blank	nd	nd	nd
Results are all semi quantitative due to not having any internal standard and not being sure of the exact volume of the extract.			

4. Discussion

A certain number of data and information is required for the estimation of contaminant fluxes. The quality of estimates of fluxes is dependent on factors such as the accuracy and precision of the measurement of the volumetric flow of water for the period of time for which the estimate is calculated and that of the methodology used for the determination of the contaminant concentrations. When total concentrations in water are determined, these can be directly multiplied by the volumetric flow of water Q (m^3 s^{-1}) and t the period for which the flux is calculated to obtain the total mass of contaminant that was released by a river into coastal areas per unit of time:

$$F_{conta\,\min ant} = t \times Q \times C_{conta\,\min ant}^{"wholewater"}$$

Bottle sampling to determine total of concentrations hydrophobic contaminants is generally characterised by poor limits of detection. It may also be significantly affected by varying levels of SPM and DOC in the water [5]. When extractions are conducted using solid phase extraction, sample filtration is often needed and sample storage in a glass bottle, analyte sorption to the filter are processes that may have a significant impact on the quality of the measurement. Since this method provides an indication of concentration at one point in time, many more samples may be needed in order to estimate mean water concentrations or for the data to be adequately used in the calculation of fluxes.

An increase in contaminant hydrophobicity is generally followed by an increase in the fraction sorbed to suspended and dissolved organic matter. Depending on the quantity of SPM and DOC in water, the largest fraction of analytes with log K_{OW} up to 5-6 is generally in the dissolved fraction, while for more hydrophobic analytes, the fraction sorbed onto particulate matter and DOC become dominant. This means that reasonably accurate estimates of fluxes may be obtained by measuring contaminant concentration only in the dissolved or in the particulate phases. When limits of detection of common bottles sampling are not low enough, alternative tools and techniques such as those evaluated here may be used to improve such limits of detection. These tools however are principally based on the measurement of specific fraction of contaminants in water (dissolved for passive sampling or the fraction of contaminants associated to suspended particulate matter in the case of continuous flow centrifugation) but may offer advantages such as integrative monitoring (with passive samplers or time-integrative suspended particulate matter samplers). Two possibilities arise. Contaminants may be monitored in various fractions in water and the sum of these fractions, for example dissolved and SPM-associated contaminant fluxes may be summed:

$$F_{conta\,\min ant} = t \times Q \times \left[C_{conta\,\min ant}^{passivesampling} + C_{SPM} C_{conta\,\min ant}^{SPM} \right]$$

However, both the accuracy and precision of this procedure are influenced by the measurement not only of Q but also of the level of SPM in water (C_{SPM}). Additional uncertainty arises from the possibility that the fraction of SPM (grain sized distribution etc) used for the measurement of contaminant concentration is different to the measurement of SPM in water. Importantly, it has also been shown that SPM levels and grain size distribution may vary spatially and with depth in river water [67]. Finally sorption of contaminants to DOC and colloids is not taken into account by this procedure and this may add further uncertainty. However, since we are dealing with extremely low contaminant concentrations (close to LODs where analytical variability is highest), the speciation of contaminants between these different fractions is difficult to measure and the uncertainty due to the affinity of contaminants to DOC and colloids remains difficult to estimate or largely unknown.

It may be possible that a reliable evaluation at a water body-specific level of the speciation or partitioning of contaminants in water results in the simplification of monitoring tasks and burden by only monitoring one single phase. Whole water concentrations may then be

modelled and fluxes calculated. Such procedure may be based on assumptions such as equilibrium partitioning between SPM/DOC and dissolved phase contaminants. A statistical understanding of the uncertainty surrounding such procedure may need developing. It may be that such uncertainty when using continuous or integrative sampling is relatively small in comparison with the use of, for example, pre-determined monthly sampling when the temporal variability in contaminant concentration in water is unknown.
In addition, the variability and uncertainty associated with the measurement of concentrations need to be put into perspective with respect to other parameters such as the accuracy of the water flow measurements as well as that of the measurement of the level of suspended particulate matter in the water [68].

4.1 Concentration and flux estimates from conventional and new approaches

Since this field evaluation aimed to assess whether some of these methods may be used for measurement trace contaminant concentrations for the estimation of fluxes of contaminants (RID programme), it is useful to start by comparing limits of detection achieved using methodologies tested here with those that would be obtained if sampling was undertaken with bottle sampling. For PAHs, LODs generally vary in the range 1-50 ng L^{-1} depending on the laboratory, procedure used for extraction and characteristics of the water sample. For PCBs and organochlorines, these are often found close to 1 ng L^{-1}; however the use of high resolution GC/MS can reduce this value to approximately 0.1 ng L^{-1}. LODs for PBDEs vary between 0.1 and 10 ng L^{-1} depending on the compound. Finally, LODs for hexabromocyclododecane are generally found at the level of a few ng L^{-1} (Table 4-1) Detection limits for these analytes at the NIVA laboratory are also in these ranges.

Table 4-1. Limits of detection (LODs) for PAH, PCBs and organochlorines, TBT and organo-tins, PBDEs and hexabromocyclodocecane (HBCD) commonly observed for bottle sampling and those from analysis at NIVA.

Analyte	Commonly observed* LOD (ng L^{-1})	"NIVA" LOD (ng L^{-1})
PAHs	10-50	2
PCBs and organochlorines	1-10 0.1 (with HR-GC/MS)	0.5
TBT/organo-tin	1	1
tetraBDE, pentaBDE, hexaBDE	1	
BDE47	0.1	
BDE99/100	0.1	
heptaBDE, octaBDE, nonaBDE	2	
DecaBDE	10	
HBCD	10	
*e.g. from: http://www.analytica.se/hem2005/eng/miljo/vatten_organiska.asp		

The following figures (Figures 4-1 to 4-6) aim to show the range of concentrations of contaminants for those where concentrations in suspended particulate matter or in the filtered/dissolved phase were above limits of detection. This set of figures also shows the range of limits of detection achieved by each method (when a range of LOD is available, the optimum value was used). Owing to the nature of this data and the processes that influence the variability and uncertainty of these methods, concentrations and limits of detection are shown on a log-transformed scale.

These figures are useful for the comparison of methods that measure operationally-defined fractions that may be mostly similar (e.g. the time-integrative SPM sampler, continuous flow centrifugation and filtration) and for the comparison of amount of analytes found in the particulate and filtered/dissolved fractions.

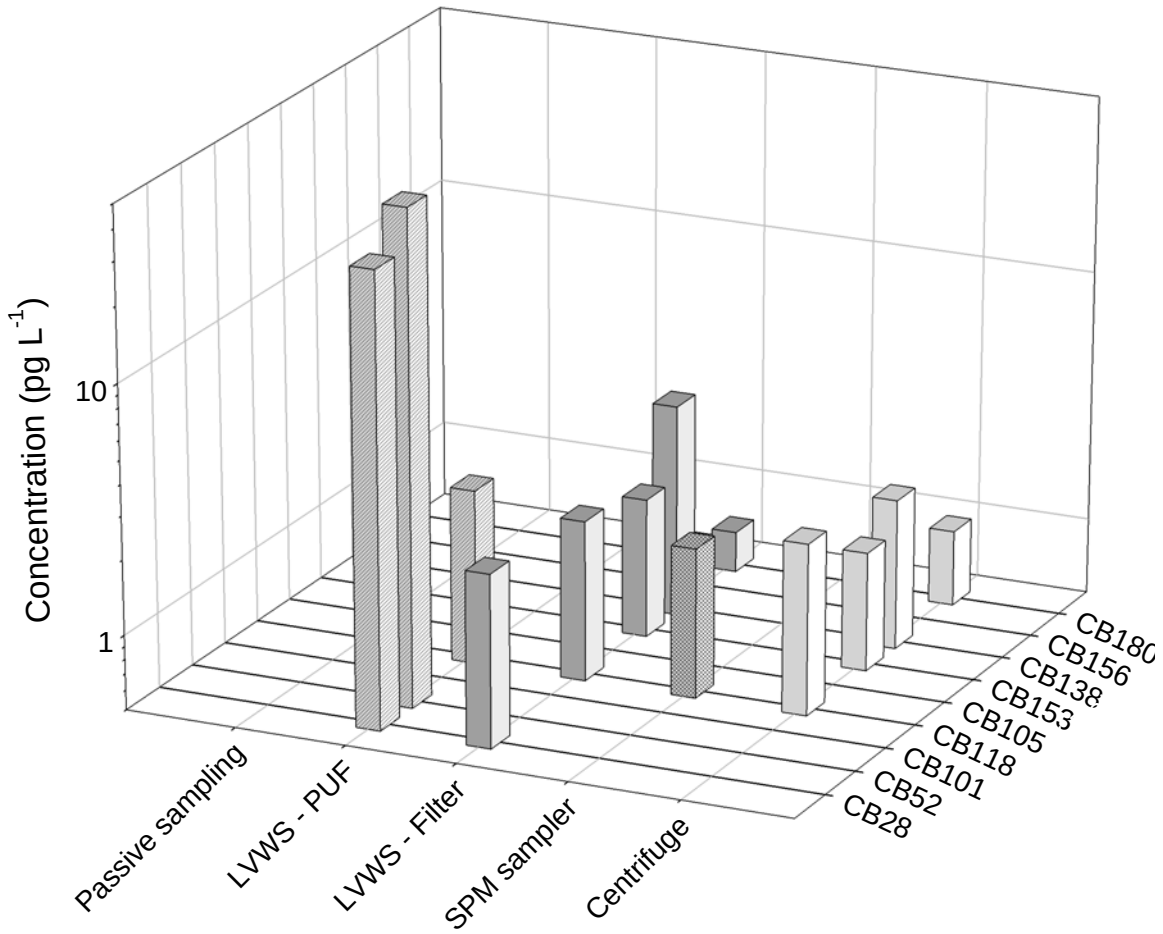

Figure 4-1. Particulate, filtered or dissolved phase concentrations of PCBs measured by continuous flow centrifugation, time-integrative SPM sampler, large volume water sampling (LVWS) and passive sampling. Note: only analyte > LOD are included in this graph. When multiple samples from one technique were > LOD, the mean of these values is plotted. If some values were < LOD, these were not taken into account. Although plotted on the same figure, note that the fraction measured by these techniques is different (particulate, filtered or dissolved) despite the same unit.

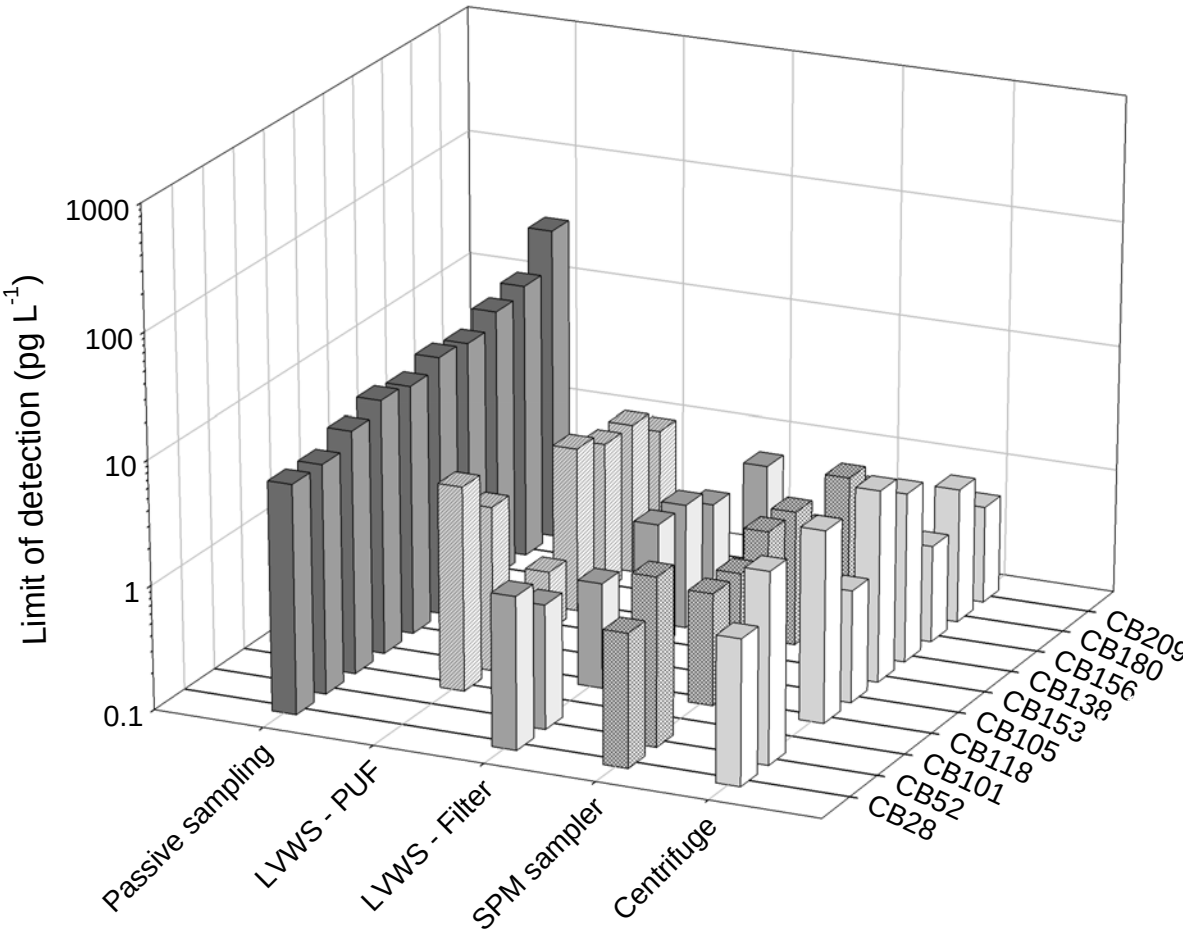

Figure 4-2. Limits of detection (pg L^{-1}) for PCBs in the particulate, filtered or dissolved phase measured by continuous flow centrifugation, time-integrative SPM sampler, large volume water sampling (LVWS) and passive sampling. Note that those with no LOD are those with all measurements > LOD. Although plotted on the same figure, note that the fraction measured by these techniques is different (particulate, filtered or dissolved) despite the same unit.

Generally PCB concentrations were low as is shown in the figure above. For analytes that were detected, concentrations measured on the SPM by all three techniques were generally similar. Large volume water sampling and the continuous flow centrifuge resulted in the highest number of compounds detected. This variability may be the result of concentrations being close to LODs. Only the least hydrophobic PCBs were found in the filtered fraction measured by large volume water sampling. Interestingly, a similar fraction of CB118 was found in the filtered and particulate fraction and more CB28 was found in the filtered phase. No PCBs were detected by SPMDs deployed for 4 weeks. As shown above, limits of detection for the SPMD devices were similar to those for filtered concentrations. In general, limits of detection for the measurements made with all methods based on SPM that were tested here were of a similar magnitude. However, it is possible that the dissolved fraction measured by passive samplers is well below that of the filtered fraction measured with PUF plugs since the filtered concentration measured with large volume water sampling may include a proportion of compound sorbed to DOC and colloids that may be retained on the PUF plugs. Overall there is agreement between the different methods and PCB concentrations are low and probably representative of conditions with minor anthropogenic impacts. PCB

concentrations on suspended sediments measured in Aire and Calder (UK) within a significantly urbanised and industrialised catchments were close to two orders of magnitude higher than those measured here [69].

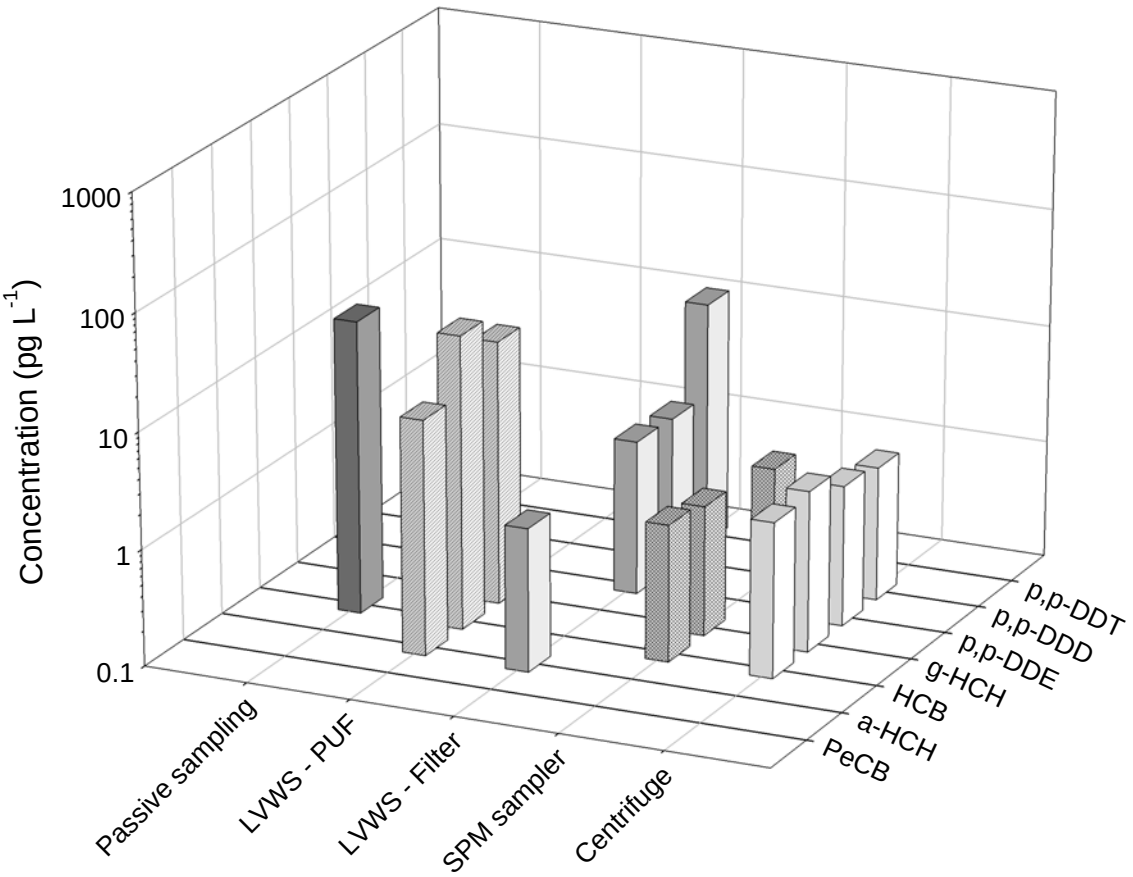

Figure 4-3. Particulate, filtered or dissolved phase concentrations of organochlorines measured by continuous flow centrifugation, time-integrative SPM sampler, large volume water sampling (LVWS) and passive sampling. Note: only analyte > LOD are included in this graph. When multiple samples from one technique were > LOD, the mean of these values is plotted. If some values were < LOD, these were not taken into account. Although plotted on the same figure, note that the fraction measured by these techniques is different (particulate, filtered or dissolved) despite the same unit.

Of all organochlorines, only hexachlorobenzene (HCB) was found above LODs using passive sampling devices while *p,p'*-DDT was only measured in the filter and PUF samples from the large volume water sampler. Excellent agreement of dissolved (from passive sampling) and filtered HCB concentrations was observed while the fraction found associated to particles tend to be lower. Limits of detection for large volume water sampling, centrifugation and time-integrative SPM sampling are in the same range close to or below 1 pg L-1. These values are also in the same range as those obtained by other workers [70] for the measurement of DDT and degradation products DDE and DDD in the particulate phase using an Infiltrex large volume water sampler in Lake Chelan, Washington. However they were able to measure

these compounds in the filtered phase (filter pore size 1 μm and XAD-2 resin for retaining analytes of interest). Here, these compounds were not detected in the filtered fraction. Combinations of filter size and resin or foam may affect retention efficiency for these analytes and affect partitioning between these operationally defined filtered and particulate phases. Limits of detection for filtered and dissolved fractions are mostly similar. The limit of detection for HCH isomers and PeCB with passive sampling is limited by the capacity of the sampler since these analytes are expected to reach equilibrium relatively rapidly and the ratio $K_{SW}V_S$ dictates LODs. The detection of HCH isomers only in the filtered fraction measured with large volume water sampling is in agreement with its relatively low hydrophobicity and HCH isomers are likely to be mostly present in the filtered fraction. As for PCB, levels of oragnochlorines measured in the Drammenselva appear very low.

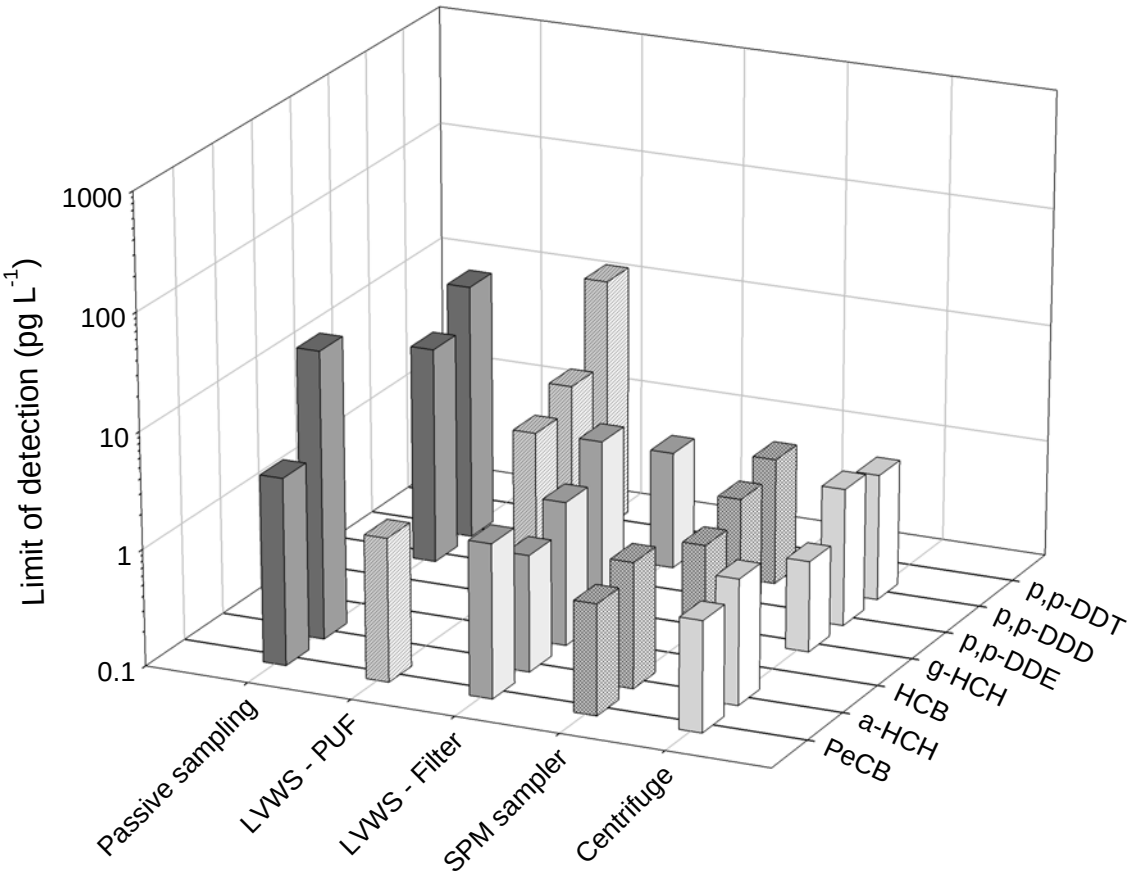

Figure 4-4. Limits of detection (pg L^{-1}) for organochlorines in the particulate, filtered or dissolved phase measured by continuous flow centrifugation, time-integrative SPM sampler, large volume water sampling (LVWS) and passive sampling. Note that those with no LOD are those with all measurements > LOD. Although plotted on the same figure, note that the fraction measured by these techniques is different (particulate, filtered or dissolved) despite the same unit.

Since PCBs and organochlorines were found at very low concentrations and very close to limits of detection, the situation is likely to be similar if not more challenging for PBDEs. Firstly, the figure below is made slightly confusing by the fact that many more BDEs were observed in one PUF sample from the large volume water sampler. In most cases apart from that specific sample, BDE47, BDE99 and BDE209 were detected with the various techniques

under evaluation here. BDEs associated to the particulate fraction and measured by the three techniques were in a similar range. The concentration of BDE209 in one filter sample was one order of magnitude higher than all others and this resulted in the mean concentration for that method close to 100 pg L^{-1}. All other measurements are closer to 10 pg L^{-1}. Streets *et al.* [71] also undertook large volume water sampling for PBDEs. Filtration of as much as 800 L of water with multiple filters was possible. PBDEs were measured in the water of Lake Michigan and concentrations were of a similar order of magnitude as those measured here. Similarly to our study they found higher levels of BDE47 and BDE99 in the filtered phase than in the particulate (using filters with identical pore size). Predicted concentrations for other Great Lakes are also in the range observed here. However, concentrations measured the Zhujiang River estuary appeared generally higher than those measured in the Drammenselva River [72]. Levels of SPM in these waters were significantly higher than in the Drammenselva and they observed lower SPM-water partition coefficient for PBDEs than we did here. PBDE partitioning in waters of the New York/New Jersey harbour was investigated and PBDE concentrations in water were significantly higher than those measured here, likely to be the result of significantly more urbanisation [73]. However, as in our study, generally higher BDE209 concentrations in the particulate phase were showed compared with those for BDE 47 and BDE99. Different salinity of the water is also likely to play a role in the speciation of these compounds.

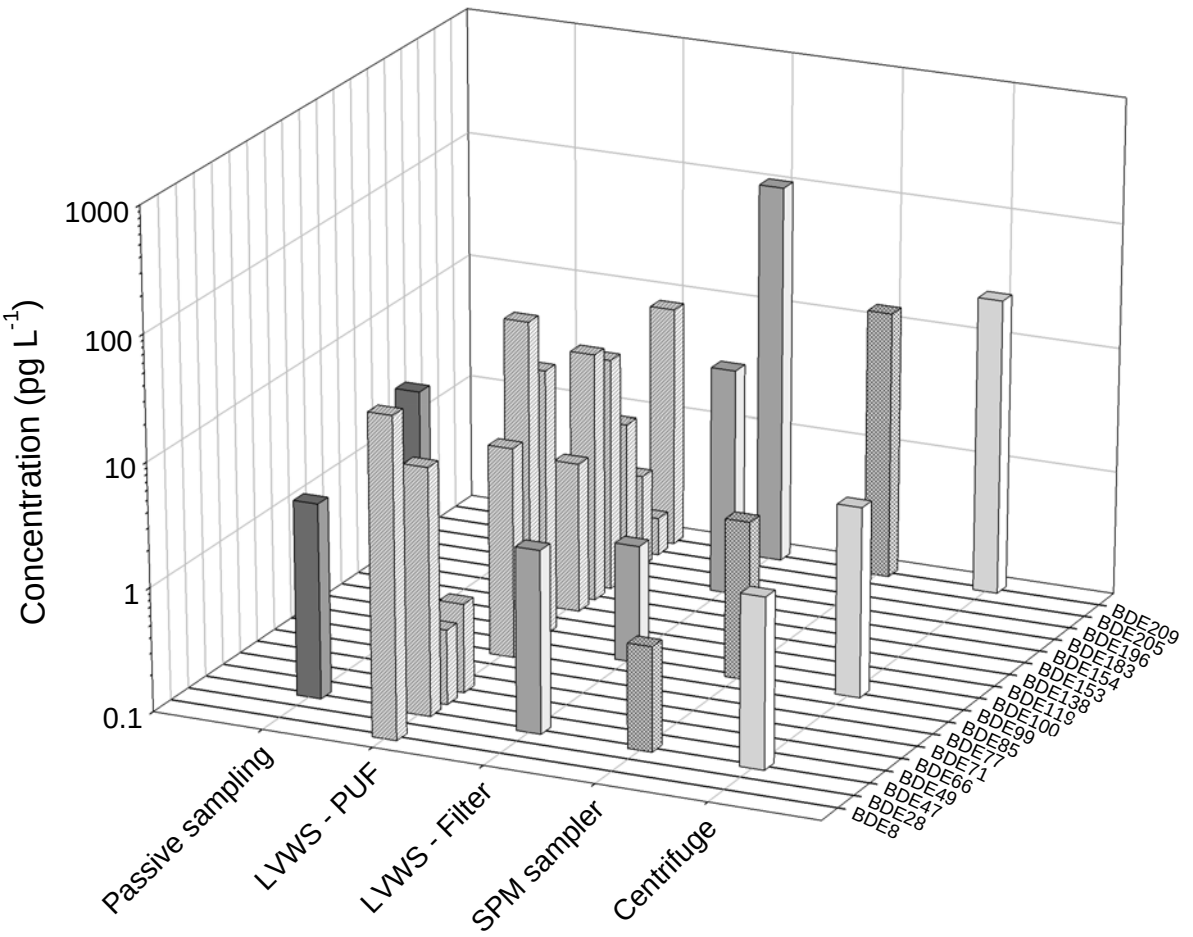

Figure 4-5. Particulate, filtered or dissolved phase concentrations of PBDEs measured by continuous flow centrifugation, time-integrative SPM sampler, large volume water sampling (LVWS) and passive sampling. Note: only analyte > LOD are included in this graph. When multiple samples from one technique were > LOD, the mean of these values is plotted. If some

values were < LOD, these were not taken into account. Although plotted on the same figure, note that the fraction measured by these techniques is different (particulate, filtered or dissolved) despite the same unit.

Limits of detection are mostly in the same range for all techniques evaluated in this study. For passive samplers, limits of detection generally varied between les than 1 pg L^{-1} and approximately 10 pg L^{-1}. Other researchers [74, 75] were able to obtain improved limits of detection by further clean-up and concentration of the extract prior to analysis with HR-GC/MS. Booij *et al.* [76] also achieved slightly better limits of detection, however these were in part due to significantly higher uptake rates during their study.

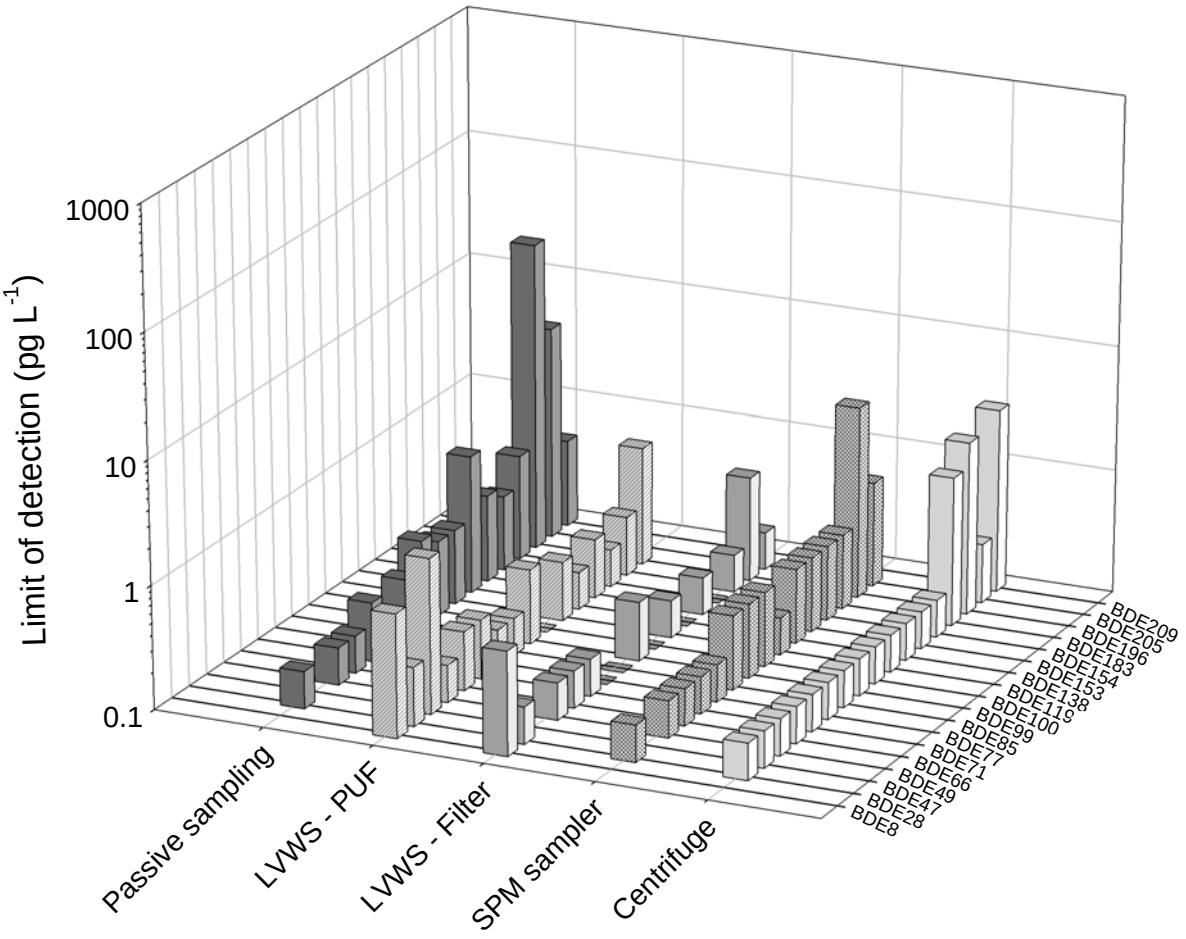

Figure 4-6. Limits of detection (pg L^{-1}) for PBDEs in the particulate, filtered or dissolved phase measured by continuous flow centrifugation, time-integrative SPM sampler, large volume water sampling (LVWS) and passive sampling. Note that those with no LOD are those with all measurements > LOD. Although plotted on the same figure, note that the fraction measured by these techniques is different (particulate, filtered or dissolved) despite the same unit.

4.2 Organic contaminant partitioning and speciation in surface waters

The characterisation of partitioning of hydrophobic organic contaminants in water is important with respect to contaminant bioavailability and water quality [4]. However, an understanding of water body specific data on contaminant partitioning may also be relevant to the measurement of concentrations for further flux estimations. When a significant proportion of a contaminant burden is present in one single phase or fraction, it may be possible to simplify monitoring and focus specifically on such phase. When contaminants are present in significant proportion in more than one fraction, the measurement of contaminant concentrations in all phases may be required. It may however, be possible in such situations to monitor only one specific phase. Total water concentrations may then be modelled and predicted if accurate knowledge of partitioning is available. Temporal variability in SPM-water partitioning (e.g. in term of seasonality, changes with water temperature and amounts of SPM in water) may also need to be well understood for such modelling to become possible [72, 73].

Data from filters and from PUF plugs were used to calculate approximate particulate organic matter-water partition coefficients for PBDE for which both the filtered and particulate concentrations are above limits of detection. These are plotted on the figure below as a function of log K_{OW}. In addition, data for which only one or the other piece of data is available are also plotted on Figure 4-7. Log K_{OC} values vary between 6 and 9 while estimates based on 1 limit of detection are in the range 4.5 and 8.5. As expected, these values appear to increase with increasing log K_{OW}. Values found in our study are in a similar range as those measured by Streets *et al.* [71] in Lake Michigan. Differences however could be explained by difference in the procedure to undertake filtration and measurements in the dissolved phase. Data from New York harbour [73] and from the Zhujiang River estuary [72] apparently show decreases in SPM-water partitioning for PBDEs with increasing SPM/POC levels. Partition coefficients found during the study in New York harbour were similar to those presented here.

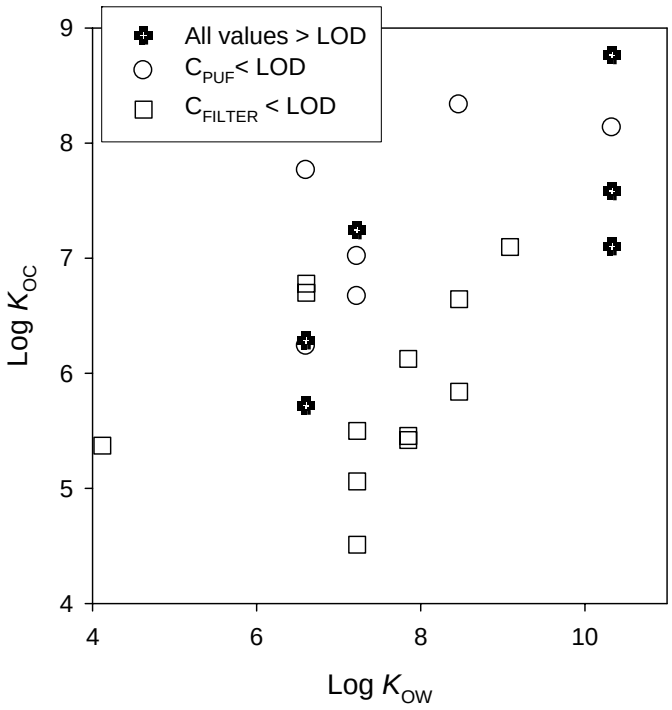

Figure 4-7 Relationship between estimated logarithm of particulate organic carbon-water partition coefficients (log K_{OC}) and logarithm of octanol-water partition coefficients (log K_{OW}) for a range of PBDEs based on large volume water sampling data for the Drammenselva River.

This procedure was repeated for PCB (Figure 4-8. It is interesting to note that values of log K_{OC} are close to log K_{OW} values. When either the filtered or particulate fraction was < limits of detection, these were also plotted. It can seen on Figure 4-8 that for analytes > log K_{OW} 5.5-6, log K_{OC}s are likely to be higher than 6.5 while for those with log K_{OW} < 6.0, log K_{OC}s are likely to be lower than 5.5-7.0.

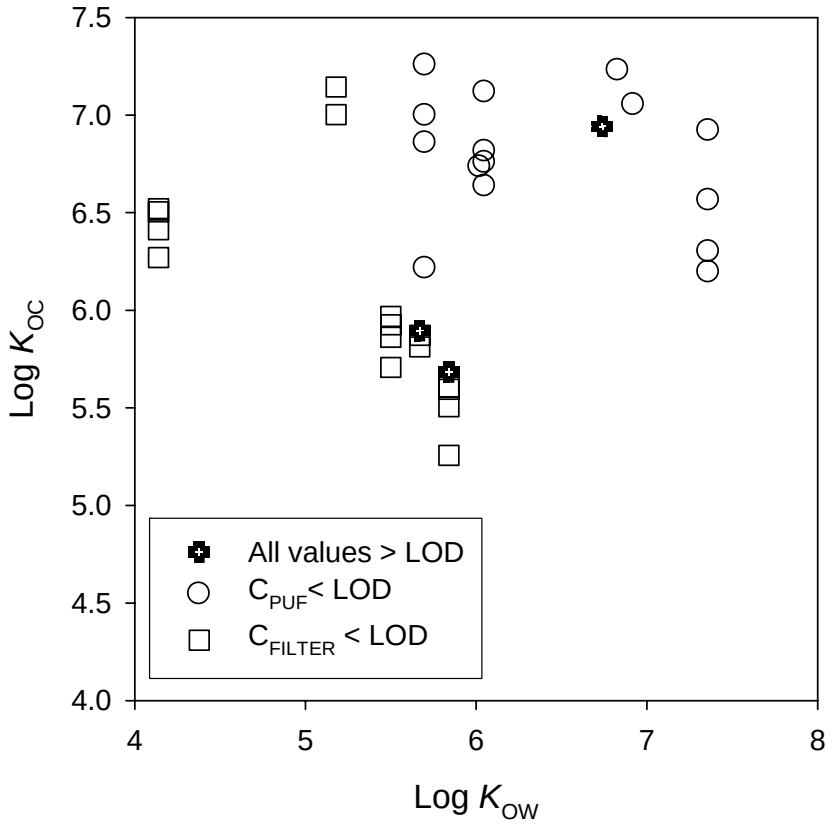

Figure 4-8. Relationship between estimated logarithm of particulate organic carbon-water partition coefficients (log K_{OC}) and logarithm of octanol-water partition coefficients (log K_{OW}) for a range of organochlorines and PCBs based on large volume water sampling data for the Drammenselva River.

Fractions not taken into account in this work include contaminants associated with dissolved organic matter and with colloids (i.e. fraction able to pass through commonly used filter sizes). Contaminant burden associated with colloids and dissolved organic matter is generally complex to determine accurately in the field since it is difficult to measure this fraction while minimising the impact of the measurement technique on contaminant distribution and partitioning [4]. Such attempts generally result in high uncertainty of the measurements.

4.3 Pros and cons of these novel approaches

Advantages and drawback of the techniques evaluated here are listed below. These were separated into those primarily based on the actual operation of the sampling technique and those related to the usefulness of the data collected and the quality of the information provided. Most techniques provide operationally-defined measurements of parameters (e.g. the use of a filter with a pore size different to the one used here may result in different values of filtered and particulate associated fractions of contaminants), and this needs to be taken into account when selecting a monitoring method.

4.3.1 Operational use and user-friendliness

For each type of monitoring procedure, pros and cons associated with the operational use and user-friendliness of the methods are provided. To a certain extend, these are applicable to

their future introduction into the RID monitoring programme. These are mostly based on our experience obtained during this field evaluation.

Pros	Cons
Passive sampling devices	
Availability of a British Standard Institute Publicly Available Specification (BSI PAS) provides guidance for passive sampler operational use	Need for relatively secure sites
Future availability of an ISO standard providing guidelines for operational use	Sometimes require creativity or ingenuity for deployment
Small size means ease of shipment, limited freezer storage space required	Often need for boat for sampler deployment since samplers exposure need to be representative of overall water conditions
Relatively simple laboratory-based extraction (simplified matrix)	Need for deployment equipment (cages, ropes, anchors, buoys etc)
	Increase in cost due to the need for control/blank samplers (for quality assurance purposes)
Large volume water sampler	
Electronic set-up of pumping rates and sample volumes	Large/heavy equipment
Most parts in contact with river water (the sample) can be solvent rinsed	Need for pre-clean filters, polyurethane foam plugs or XAD resin
Robust sampling equipment	Possibilities for contamination
Continuous flow centrifugation	
Very simple equipment to use, robust	When SPM levels in water are low, extended sampling times often require secure sites with electrical power
Possibility of using a generator for use in remote sites	Use of tubing to bring river water to the centrifuge limits the distance between the centrifuge and the water sampling point in the river
Sampling times may vary from hours to days	Need for a peristaltic pump
At a secure site, the centrifuge may be left unattended for extended periods of time.	Laborious SPM removal from the centrifuge drum when SPM amount is small (sometimes need use of filtration of water left in the drum following sampling)
Possibilities to clean all equipment prior to sampling (including the stainless steel drum)	
Time-integrated suspended particulate matter sampler	
Different sampler size may be produced depending on the type and conditions of rivers	Heavy (when full of water) and large devices difficult to operate
May be exposed for periods of weeks to months	Require creativity or ingenuity for deployment
May be left unattended	Often need for boat for sampler deployment since samplers exposure need to be

	representative of overall water conditions
	Use of the continuous flow centrifuge to collect SPM from the samplers with possibilities for further sample contamination
	Challenging sampler cleaning and blank issues
	Possibilities of clogging of the narrow inlet/outlet tubes during exposure
	Difficulty in retrieving SPM from the samplers
SCF	
Simple principle and relatively simple operation	Results may be strongly affected by the fieldworker in charge of manipulation and sampling
Rapid on site operation	

4.3.2 Data use and data quality

Some of the issues related here may not be specific to a particular method but may be related to how a representative sample is collected using different methods.

Pros	Cons
Passive sampling devices	
Time integrated measurements over periods of weeks to months	Relatively complex procedure to estimate dissolved contaminant concentrations in water
Measurement of dissolved concentrations (representative of water quality)	Uncertainty in K_{SW} values; when using one single type of sampler, this may be considered as bias of the method
Information on contaminant speciation in water	Unknown effects of biofouling
Low variability when using one single type of sampling devices (so very useful for water quality measurements and for the assessment of temporal trends)	Uncertainty in the mode of calculation of time-weighted average concentrations
Lower analytical uncertainty owing to simplified matrix composition	
Low limits of detection (low pg L^{-1} range) but these vary with exposure time, type of analyte, environmental conditions	
Large volume water sampler	
Separation of the measurement: SPM-associated and filtered (dissolved?) contaminants, enabling estimation of contaminant speciation with the use of one technique	Data and information obtained are valid for one moment in time only, repeated sampling is needed for temporal information
Possibility to achieve low limits of detection owing to the large volumes of water	Difficulty in producing adequate blanks and controls

extracted	
	Recoveries for various contaminants may be uncertain (filter and PUF plugs)
	Uncertainty with regards to the fate of DOC/colloid-bound contaminants
	Potential for sorption of dissolved contaminants to the filter
Continuous flow centrifugation	
Limits of detection for river water generally in the low pg L^{-1}	Sampling may differ depending on grain size distribution in river, centrifuge rotation speed and water flow into the centrifuge
Sampling may be optimised to sample most SPM	Limits of detection dependent on levels of SPM in water and SPM mass needed for analysis
	Variability associated with SPM extraction and analysis
	Not only sediment but plant debris and other organic matter may be collected
	SPM grain size distribution in river may vary with depth in the river and along the river transect and lead to unrepresentative sampling
	Uncertainty in contaminant (re)partitioning between accumulated SPM and water in the sampler during sampling
Time-integrated suspended particulate matter sampler	
Limits of detection for river water generally in the low pg L^{-1}. These are of a similar level to those for continuous flow centrifugation	Variability associated with SPM extraction and analysis
Time-integrated sampling over periods of weeks to months	Not only sediment but plant debris, organic matter
Ability to sample of fine grained suspended sediments	SPM grain size distribution in river may vary with depth in the river and along the river transect and lead to unrepresentative sampling
	Uncertainty in sampling due to clogging
	Uncertainty in contaminant (re)partitioning between accumulated SPM and water in the sampler during sampling
SCF	
Provides estimate of total, filtered and ion exchanged fractions of metals in water	Variability in the results, possibly due to the manual filtration step
Information of contaminant speciation	

As a conclusion, the reliability of the data may be significantly improved by the use of multiple techniques alongside. However, this results in significant monitoring burden and cost.

4.3.3 Challenges and how to address them

The following table present some of the possibilities for addressing some of the drawbacks identified in the previous sections. In addition, these possibilities would certainly help in reducing the uncertainty and variability of the measurements undertaken with these methods.

Challenges	Possibilities
Passive sampling devices	
Improve limits of detection	-Optimise the ratio for splitting extracts between the PRC fraction and that for PBDEs and PCBs, since PRC limits of detection may not need to be as high as those for PBDEs -reduce extract volume and use of HR-GC/MS -Increase water turbulences around the samplers to maximise uptake rates -Develop/optimise cages for exposure -Increase exposure duration
Contamination of blank/control silicone strip samplers	-Additional solvent clean-up of samplers -Minimise time samplers are exposed to the air in the lab following the initial clean-up stage
Uncertainty in the sampling of PBDEs with passive samplers (boundary vs. membrane control of the uptake)	-Measure K_{SW} and D_m values for PBDEs in the different materials -Use of field site with higher PBDE levels in water
High uncertainty of log K_{OW} values for PBDEs	-Extrapolation of uptake rates using alternative molecular descriptors
Bias and uncertainty of using different types of sampling devices	-Use of only one type of samplers may reduce variability and help investigating trends -Bias due to uncertainty of sampler-water partition coefficients for example is more difficult to address.
Is membrane control of the uptake rate for large molecules the reason for detection of HBCD in silicone strips and not in LDPE membranes in the Alna river?	-Repeat such study at a site with higher levels of HBCD for example
Uncertainty in the mode of calculation of time-weighted average concentrations	-Calculating time-weighted average concentrations using different models and assumption may provide a range of concentrations that may be of use
High Hg contamination of gels in DGTs	-Add a procedure to further clean Hg contamination remaining in the sampler following production
Large volume water sampler	
Recoveries and extraction efficiency for PUF plugs	Use of spiked reference/recovery standards for PUF plugs

Continuous flow centrifugation	
Quality control of sample collection and grain size distribution	-Assessment of SPM grain size distribution in water from inlet/outlet of the centrifuge
Uncertainty in recoveries of contaminant extraction from the SPM material	- Collect SPM from various rivers for use inr spike-recovery work with deuterated, ^{13}C, ^{14}C or fluoro standards for example
Potentially low levels of SPM that may be sampled	-Increase sampling duration, size of the centrifuge and processing capacity -Develop a secure but mobile set-up that may be left unattended for days next to a river
Uncertainty of procedure for collecting SPM from the centrifuge drum	-Increase SPM amounts accumulated so that this step does not influence the final measurement
Time-integrated suspended particulate matter sampler	
Sampler deployment	-Permanent or semi-permanent static systems for SPM sampler -Anchor/buoy system for deployment
Uncertainty in recoveries of contaminant extraction from the SPM material	- Collect SPM from various rivers and use it for spike-recovery work with deuterated, ^{13}C, ^{14}C or fluoro standards
Simplify operation of the sampler	-Simplify opening and closing of the sampler -Use of an conical shaped recipients for collecting SPM after settling in the device and removal of excess water
Sampler preparation and cleaning prior to deployment	
SCF	
Results may be strongly affected by the fieldworker in charge of manipulation and sampling	-Mechanical or automatic sample processing

5. Conclusions

5.1 Detailed conclusions about this field evaluation

The measurement of contaminant fluxes associated with rivers is an important task as part of a number of regulatory monitoring programmes. The quality, in terms of accuracy and precision, of *average contaminant concentrations* is therefore very important for adequate estimation of fluxes.
This study was conducted with the aim of developing sampling and analytical methodologies to improve the measurement of contaminant concentrations in water used for further estimation of contaminant fluxes in rivers. These techniques are based on the monitoring of (operationally-defined) specific fraction of contaminants in water. These include fractions associated with suspended particulate matter, dissolved in water or labile to specific tools. In addition, some of these techniques provide information and data for one specific moment in time (at the time of sampling) while others allow time-integrated information on concentration level to be obtained. In general these techniques are able to provide improved limits of detection compared with those commonly achieved with bottle sampling. These aspects are particularly important for the RID monitoring programme. It is hoped that this work lays the foundation for the future use of some of these techniques to improve estimates of the contribution of contaminant fluxes from rivers in Norway to the contaminant burden in the sea.
Objectives of this study were therefore to evaluate the performance of several methods for the sampling of hydrophobic organic contaminants and metals in the Drammenselva River. These included the sampling of particulate-associated contaminants *via* continuous flow centrifugation, time-integrated suspended particulate matter sampling and filtration during large volume water sampling. Analysis included the measurement of PCBs, PBDEs, organochlorines and PFCs. Sampling of dissolved phase contaminants was undertaken using three types of passive sampling devices, namely semipermeable membrane devices (SPMDs), low density polyethylene membranes and silicone strips produced in house, and with large volume water sampling. Compounds of interest were PAH, PBDE, PCBs, organochlorines and organotins. DGT samplers were deployed to measure the labile fraction of trace metals and results were compared with WHAM speciation modelling in an attempt to understand and predict the fraction of metals sampled by DGT. SCF fractionation was also undertaken.
Screening of extracts from passive samplers for pharmaceuticals was conducted and semi-quantitative work was undertaken using extracts from passive sampling to measure hexabromocyclododecane.
Additional proof-of-concept work was conducted by exposing LDPE and silicone samplers in the Alna River for the monitoring of PBDEs and of different types of DGTs in the Akerselva River.

This study focussed on the monitoring of many organic contaminants with a number of methods and this allows us to make a number of conclusions regarding general levels of contamination in the Drammenselva River:

- In all cases, levels are low and this is demonstrated by concentrations close to limits of detection at the low or below pg L^{-1} level.
- Generally low concentrations of PBDEs were found. BDE47, BDE99 and BDE209 were the brominated flame retardant commonly found in most samples. Concentrations either dissolved (or filtered) and in the particulate were between < 1 pg

L^{-1} and as high as a few tens of pg L^{-1}. SPM concentrations of BDE209 were consistently higher than those measured for other BDEs.

- Perfluoroalkyl compound extraction from SPM samples was successfully conducted and only two compounds were detected at levels barely above limits of detection, resulting in low pg L^{-1} levels in water.
- PCBs in the dissolved phase were below 10-20 pg L^{-1} as measured by SPMDs. Large volume water sampling enabled consistent quantification of CB28 and CB52 (and with low variability) at concentration slightly above LODs for passive samplers. This is not surprising since a significant proportion of these compounds is present in the dissolved fraction under these specific environmental conditions. The discrepancy between passive sampling and large volume water sampling may be the result of retention of DOC and colloidal-bound PCBs by the PUF plugs.
- Some organochlorines were detected at low levels in the particulate phase with concentrations in the approximate range 1-20 pg L^{-1}. HCH isomers were also found in the filtered fraction between 10-20 pg L^{-1}.
- Screening with POCIS passive samplers showed that only paracetamol and carbamazepine were detected in the extract. It is likely that the concentration in water is around a few ng L^{-1}, indicating that sewage contribution to the river is minor.
- PAH concentrations measured by passive sampling devices are low, only the concentration of phenanthrene was above 1 ng L-1 (which represent the LOD of a reasonably performant bottle sampling analytical scheme).
- Of all organotins, only TBT and TPhT concentrations can be reasonably estimated with SPMDs. Concentrations were < LOD for both consecutive exposures (with LOD ~ 0.02-0.1 ng L^{-1}).

This study also provided a comprehensive dataset focussing on furthering our understanding of the principles of passive sampling for hydrophobic organic contaminants. This work primarily aimed to evaluate the performance of three types of samplers made of different polymeric materials, but with similar surface areas. The aim was to evaluate with similar levels of information could be obtained with all three types of samplers and whether more user-friendly single polymeric samplers could replace the use of SPMDs. Similar sampler surface areas and canister deployment help in concluding that:

- The use of performance reference compounds (PRCs) was successful with all three samplers.
- After normalisation to sampler surface area to volume ratio, PRC elimination rates obtained were in excellent agreement.
- Slopes of log $k_{e\text{-}PRC}$-log K_{OW} relationship for all three sampler are between -0,7 and -1 and similar to data obtained by [19].
- PRC data appears to demonstrate that uptake for analytes with log K_{OW} > 4-4.5 is limited by mass transfer in the boundary layer at the surface of the sampler.
- This is further confirmed by practically identical masses of analyte under boundary layer controlled uptake (and linear uptake mode) absorbed by the samplers irrespectively of the sampler material used (this stands as long as the capacity of sampling material is high enough) for exposure of 24 and 51 days.
- Ratios of masses absorbed for PAHs under boundary layer controlled and linear uptake regime for exposure of 24 and 51 days are consistent.
- Relatively low sampling rates were achieved and are in agreement with a cut-off point between membrane and boundary layer control of the uptake for analytes with log K_{OW} just over 4.

- Time limits for integrative sampling ranged from < 10 days for analytes with log K_{OW} of 3.5 to 4.0 and > 100 days for analytes with log K_{OW} of 6.
- Generally similar limits of detections were found for all samplers. For LDPE membranes, LODs were higher for analytes that were close to equilibrium due to the smaller volume of the sampler.
- Within sampler type variability was excellent both for preparation controls (based on PRC spiking data) and for exposed samplers.
- Variability in time-weighted average concentrations measured by the different samplers was within a factor of 2 to 3. This is partly due to the uncertainty and variability in sampler-water partition coefficients and in the use of PRC elimination rates. The use of the SPMD model rather than boundary layer controlled uptake model is likely to increase the divergence between concentrations measured by different samplers.
- Excellent consistency between 24 and 51 day exposures was seen, however, the longer exposure resulted in lower LODs and the detection of more PAHs (for those under linear uptake).
- The variability observed for sampling with the use of a single type of passive sampling device is likely to be significantly lower that what may be achieved when using bottle sampling for such low concentrations (especially when levels of SPM are high).

A methodology for using passive sampler extracts for the analysis for brominated flame retardants (PBDEs) was developed and extracts from SPMDs, LDPE membranes and silicone strips were screened:

- Limits of detection for PBDEs in sampler extracts were 30-500 pg per sampler.
- All PBDE were below limits of detection for blank/control LDPE membrane samplers. Some PBDEs were found in blanks/control samples for SPMDs.
- Contamination of blanks/control sampler was observed for silicone strips.
- Generally only BDE47 and BDE99 could be seen just above limits of detection or significantly above blank levels Concentrations measured by the different types of samplers were close to 1 pg L^{-1}.
- This is very promising and a number of possibilities exist to (i) lower limits of detection in the laboratory, (ii) decrease contamination levels in silicone samplers and (ii) increase uptake rates during exposure.

This study is one of very few extensive performance evaluations for so many techniques for the measurement of trace organic contaminants in water. It also covered a relatively wide range of analytes since data was generated for PAHs, PCBs, PBDEs, organochlorines.

- Limits of detections for SPM sampling techniques were in the same order of magnitude and were dependent on the actual amount of SPM collected
- Limits of detection for the methods tested here are in agreement with published data and literature where limits of detections were achieved using similar techniques
- Limits of detection were generally between 2 to 3 orders of magnitude lower than those that could be achieved with bottle sample. Simply, as exemplified for contaminants below limits of detection for both bottle sampling and methods tested here, this translates to a decrease in the flux estimate (or below) for the Drammenselva from 10 kg $year^{-1}$ (for a compound with LOD of 1 ng L^{-1}) to 10 g $year^{-1}$ (with an LOD of 1 pg L^{-1}) when the flow is 300 m^3 s^{-1}.
- When detected, analytes were generally close to limits of detection where analytical variability is highest. However, consistent concentrations of contaminants were generally observed for SPM sampling.

- Longer exposures of the time-integrative SPM sampler (assuming clogging is not an issue) is likely to result in higher amount of SPM accumulated.
- Excellent agreement between hexachlorobenzene concentrations measured by passive sampling and by large volume water sampling was seen. Uncertainty or variability associated with the mode of calculation of SPMD concentration or caused by DOM and colloids for large volume water sampling is unlikely to cause differences over an order of magnitude.
- Compatibility of analysis for HBCD and passive sampler or SPM extraction. However, methods need optimising in order to ameliorate limits of detection.
- Log transformed particulate organic carbon-water partition coefficients (log K_{OC}) calculated for some PBDEs and PCBs demonstrated that measurements made here were in the correct order of magnitude. Comparison with very scarce literature data supports our data.

DGT and SCF measurements were undertaken to evaluate trace metal concentrations in different fractions in water.

- Both techniques offer useful information on metal speciation.
- Much of the results by these two techniques can be explained by metal speciation modelling.
- The two types of DGTs tested gave similar results.
- The paper-based sorbent layer is a promising further development in DGT technique as it may be easier to handle than the gel layer.
- "reverse" modelling of total concentration based on DGT data may be a possible solution to the simplify monitoring of trace metals to determine fluxes from a single type of measurements.

The testing of DGT samplers with different types of diffusion gels and receiving phases were tested here. Standard DGTs were deployed in the Drammenselva while 3 types were used during evaluation in the Akerselva:

- Significant Hg contamination was found in blank samplers prepared with an agarose diffusion gel layer and a spheron-thiol resin gel and Hg accumulation during exposure was not significant. Water temperature during deployment in the Akerselva may have had an impact on accumulation rates.
- Significant accumulation could be seen with standard DGTs in the Akerselva, however these must have been high concentrations at the site and the use of such device for monitoring purposes at environmentally relevant conditions may not be possible.
- No clear pattern in Hg accumulation DGTs from the Drammenselva could be seen.
- Improvements in blank samplers are needed before these can be used for monitoring. A number of possibilities exist.

Information and data available in the literature appear to substantiate the use of SPMD samplers for the monitoring of TBT in water. Here, SPMD extracts were analysed for a range of organotin compounds:

- No organotins were detected despite LODs in the range of 20-100 pg L^{-1}.
- Despite higher LODs, the Chemcatcher sampler device appears promising since it allows monitoring of a wider range of organotins than SPMDs. These include MBT and DBT as well as TBT and TPhT.

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. It will also be important in the future to consider the value of information collected when sampling is continuous such as with passive samplers and time-integrated SPM sampling compared with techniques that provide data for one particular moment in time. Therefore the design of future monitoring studies may need to address such an issue and sampling frequency may need to be adapted accordingly. It is likely that the issue of sampling design and frequency has an impact as or more significant than the uncertainty associated with the analytical measurement (especially when considering aspects such as simplified passive sampler extract matrix). Finally for these techniques to be used as part of monitoring strategies such as for the RID programme, costs and operational practicalities for their implementation in different rivers across Norway will be two critical factors.

5.2 Main conclusions

A thorough evaluation of several techniques for the measurement of trace organic and metal contaminants in river water was undertaken in the Drammenselva River in 2008. This measurement of contaminant concentrations is aimed at estimating fluxes of contaminants to coastal areas associated with river flow. Rather than focussing on "whole water" samples, many of these techniques are based on the monitoring of specific fractions of contaminants present in river water (dissolved or bound to particulate matter for example). Overall conclusions of this work are:

- Most techniques based on the collection of suspended particulate matter offer limits of detection in the low pg L^{-1} concentration range.
- Techniques based on the monitoring of dissolved or filtered contaminant concentrations were also in the pg L^{-1} range with passive samplers offering the advantage of integrative sampling for up to period of 50 day or more.
- Passive sampling with low density polyethylene membranes or silicone strips offer equivalent information to that obtained with semipermeable membrane devices for the monitoring of PAH and PBDEs. In house production of these samplers offer advantages such as control and improvements of blank samplers, use of appropriate or specific performance reference compounds (PRCs). Variability of PAH concentrations measured by the three types of samplers was a factor of 2 to 3. This variability is likely to be associated with the mode of estimation of uptake rates fro PRC data and variability in sampler-water partition coefficients (K_{SW})
- Comparable data was obtained with most of the methods tested here, and when possible logarithms of particulate organic carbon-water partition coefficients (log K_{OC}) were found to be similar to those found in the literature.
- Variability in the data (when concentrations were above limits of detection) was likely due to (i) concentrations close to limits of detection when analytical variability is highest, (ii) variability in contaminant concentrations in water during the field test, and (iii) differences in results from techniques based on discrete and those using continuous/integrative sampling strategies.
- Monitoring of trace metals with DGT and SCF was mostly in agreement with speciation modelling undertaken to understand partitioning of trace metals between different fractions in water.
- Improvements in the operation of some of these techniques are needed while others may be optimised to ameliorate limits of detection and quality of blanks and controls. Possibilities are proposed.

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7. Appendices

7.1 Characteristics of PAHs and deuterated PAHs

	Log K_{OW}	MW (g mol^{-1})	V_{LeBas} (cm^3 mol^{-1})	TSA (Å)
ACE-d_{10}	3.92*	164.2		
FLUE d_{10}	4.18*	176.2		
PHE d_{10}	4.57*	188.2		
FLUO-d_{10}	5.22*	212.3		
CHRY-d_{12}	5.86*	240.3		
BeP-d_{12}	6.05*	264.3		
ACY	4.00	152.2	165.7	193.60
ACE	3.92	154.2	173	180.8
FLUE	4.18	166.2	188	194
DBTHIO	4.49			
PHE	4.57	178.2	199	198
ANT	4.54	178.2	197	202.2
FLUO	5.22	202.3	217	218
PYR	5.18	202.3	214	213
B*a*A	5.91	228.3	248	244.3
CHRY	5.86	228.3	251	241
B*bj*F	5.90	252.3	268.9	266
B*k*F	5.90	252.3	268.9	266
B*e*P	6.05	252.3		
B*a*P	6.04	252.3	263	256
Per	6.25	252.3		
In*123cd*P	6.50	276.3	283.5	
DB*ah*A	6.75	278.3	300	286.5
B*ghi*P	6.50	276.3	277.5	266.9

7.2 Characteristics of PCBs

	Log K_{OW}	MW (g mol^{-1})	V_{LeBas} (cm^3 mol^{-1})	TSA (Å)
CB28	5.67	257.8	247.3	230.83
CB52	5.84	292.0	268.2	235.84
CB101	6.38	326.4	289.1	251.62
CB118	6.74	326.4	289.1	262.04
CB105	6.65	326.4	289.1	259.41
CB153	6.92	360.9	310.0	267.39
CB138	6.83	360.9	310.0	264.76
CB156	7.18	360.9	310.0	275.01
CB180	7.36	395.3	330.9	280.37
CB209	8.26	498.7	393.6	
PeCB	5.18	250.3		
α-HCH	3.81	290.85		
HCB	5.5	284.8		
γ-HCH	4.14	290.85		
p,p'-DDE	5.7	318.1		
p,p'-DDD	6.02	320.1		

7.3 Characteristics of PBDEs

	Log K_{OW}*	MW (g mol^{-1})
BDE28	5.983	406.9
BDE49	6.604	485.8
BDE71	6.604	485.8
BDE47	6.604	485.8
BDE66	6.604	485.8
BDE77	6.604	485.8
BDE100	7.225	564.7
BDE119	7.225	564.7
BDE99	7.225	564.7
BDE85	7.225	564.7
BDE154	7.846	643.6
BDE153	7.846	643.6
BDE138	7.846	643.6
BDE183	8.467	722.3
BDE196	9.088	801.4
BDE205	9.709	880.4
BDE209	10.33	959.2
*From (and modelled from) ref. [65]		

7.4 Sampler-water partition and polymer diffusion coefficients for PAHs

	Log K_{OW}	Log K_{SW} (L kg^{-1}) Silicone*	Log K_{SW} (L kg^{-1}) Silicone**	Log K_{MW} (L L^{-1}) LDPE***	Log D (m^2 s^{-1} @ 20°C)* Silicone	Log D (m^2 s^{-1} @ 20°C)* LDPE
ACE-d_{10}	3.92			3.59	-10.05	-12.34
FLUE d_{10}	4.18			3.84		-12.09
PHE d_{10}	4.57	4.06		4.22	-10.24	-12.38
FLUO-d_{10}	5.22	4.56		4.85		-12.70
CHRY-d_{12}	5.86	5.21	5.15	5.48	-10.60	-13.30
BeP-d_{12}	6.05	5.58	6.29	5.66		-13.69
ACY	4.00	3.26	3.39	3.67	-10.07	-12.26
ACE	3.92	3.62	3.84	3.59	-10.04	-12.36
FLUE	4.18	3.79	3.89	3.84	-10.06	-12.29
DBTHIO	4.38		4.04	4.04		
PHE	4.57	4.11	4.18	4.22	-10.18	-12.45
ANT	4.54	4.21	4.31	4.19	-10.18	-12.36
FLUO	5.22	4.62	4.45	4.85	-10.40	-12.70
PYR	5.18	4.68	4.49	4.81	-10.40	-12.82
B*a*A	5.91	5.32	5.42	5.52	-10.61	-13.28
CHRY	5.86	5.25	5.23	5.48	-10.61	-13.28
B*bj*F	5.90	5.74	6.33	5.51	-10.79	-13.70
B*k*F	5.90	5.74	6.25	5.51	-10.79	-13.70
B*e*P	6.05		6.12	5.66		
B*a*P	6.04	5.69	6.27	5.65	-10.77	-13.72
Per	6.25		6.02	5.86	-10.73	-13.74
In*123cd*P	6.50	6.06	7.48	6.10	-10.94	-13.70
DB*ah*A	6.75	6.24	6.76	6.34	-10.98	-13.69
B*ghi*P	6.50	6.02	6.63	6.10	-10.92	-13.75
*From [19]						

**From [21]
***From K. Booij, personal communication

7.5 Sampler-water partition and polymer diffusion coefficients for PCBs

	Log K_{OW}	Log K_{SW} (L kg^{-1}) Silicone*	Log K_{SW} (L kg^{-1}) Silicone**	Log K_{MW} (L L^{-1}) LDPE***	Log D (m^2 s^{-1} @ 20°C)* Silicone	Log D (m^2 s^{-1} @ 20°C)* LDPE
CB28	5.67	5.53	4.79	5.29	-10.13	-12.51
CB52	5.84	5.80	5.04	5.46	-10.44	-12.88
CB101	6.38	6.28	5.93	5.98	-10.52	-13.06
CB118	6.74	6.42	6.16	6.33	-10.55	-13.05
CB105	6.65	6.42	5.60	6.24	-10.50	-13.02
CB153	6.92	6.72	6.30	6.51	-10.57	-13.28
CB138	6.83	6.77	6.52	6.42	-10.59	-13.28
CB156	7.18	6.72	7.26	6.76	-10.60	-13.34
CB180	7.36	6.99	6.61	6.93	-10.62	-13.57
CB209						
PeCB						
α-HCH						
HCB					-10.12	-12.68
γ-HCH						
p,p'-DDE						
p,p'-DDD						
*From [19]						
**From [21]						
***From K. Booij, personal communication						

7.6 Model to calculate C_{TWA} from SPMD data [14]

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

$$C_{TWA} = \frac{m}{K_{SW} V_S (1 - e^{-\frac{R_S}{K_{SW} V_S} t})} \quad (1)$$

where m is the mass of contaminant accumulated in SPMDs (ng), K_{SW} the sampler-water partition coefficient (L L^{-1}), V_S the volume of the sampler (L), t the exposure time (h) and R_S the uptake rate (L h^{-1}).

The determination of in-situ uptake rates for each site was undertaken using performance reference compounds (PRCs), deuterated analogues of PAHs. Since mass transfer in/out of the sampler is an isotropic phenomenon, first-order offload rates, k_e of deuterated PAHs spiked into the samplers prior to exposure can be used to estimate uptake rates for PRC:

$$R_S = K_{SW} V_S k_e \quad (2)$$

An empirical log K_{OW}-R_S relationship is then used to extrapolate uptakes rates for all other contaminants of interest. R_S values for compounds with log K_{OW} in the range 3-8 can then be calculated:

$$R_{S,i} = R_{S,PRC} \frac{\alpha_i}{\alpha_{PRC}} \quad (3)$$

where α can be obtained with the following empirical relationship:

$$\log \alpha = 0.013 \log^3 K_{OW} - 0.3173 \log^2 K_{OW} + 2.244 \log K_{OW} \quad (4)$$

The α value for the analyte of interest and for the PRC may be calculated using equation (4) to allow the estimation of $R_{S,i}$ with equation (3). Once the uptake rate is known, equation (1) is used to calculate TWA concentrations.

7.7 List of acronyms

This list only includes compound's full names and acronyms in the text. Acronyms used in equations are not included.
They are provided in alphabetical order.

ACY	Acenaphthylene
ACE	Acenaphthene
ANT	Anthracene
B*a*A	Benzo[a]anthracene
B*a*P	Benzo[a]pyrene
B*bj*F	Benzo[b/j]fluoranthene
B*e*P	Benzo[e]pyrene
B*ghi*P	Benzo[ghi]perylene
B*k*F	Benzo[k]fluoranthene
CHRY	Chrysene
DBT	dibutyltin
DBTHIO	Dibenzothiophene
DB*ah*A	Dibenzo[a,h]anthracene
p,p'-DDD	p,p'-Dichlorodiphenyl dichloroethane
p,p'-DDE	p,p'-Dichlorodiphenyldichloroethylene
p,p'-DDT	p,p'-Dichlorodiphenyltrichloroethane
dw	Dry weight
FLUE	Fluorene
FLUO	Fluoranthene
GC	Gas chromatography
HBCD	Hexabromocyclododecane
α HCH	α Hexachlorocyclohexane
HCB	Hexachlorobenzene
γ HCH	γ Hexachlorocyclohexane (lindane)
In*123cd*P	Indeno[1,2,3-cd]pyrene
K_{OC}	Organic carbon-water partition coefficient
K_{OW}	Octanol-water partition coefficient
LDPE	Low density polyethylene
LOD	Limit of detection
LOQ	Limit of quantification
LVWS	Large volume water sampler
MBT	monobutyltin
PAH	Polycyclic aromatic hydrocarbon
PBDE	Poly brominated diphenyl ether
PCB	Polychlorinated biphenyl
PeCB	Pentachlorobenzene
Per	Perylene
PFBS	perfluorobutane sulfonate
PFC	Perfluoroalkyl compounds
PFHxA	perfluorohexanoic acid
PFHpA	perfluoroheptanoic acid
PFOA	perfluorooctanoic acid
PFNA	perfluorononanoic acid
PFOS	perfluorooctane sulfonate
PFOSA	Perfluorooctane sulphonamide
PHE	Phenanthrene
PYR	Pyrene
POCIS	Polar organic compound integrative sampler
PUF	Polyurethane foam
SPM	Suspended particulate matter
SPMD	Semiperemable membrane devices
TBT	Tributyltin
TPhT	Triphenyltin
TWA	Time weighted average

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Tittel - norsk og engelsk

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

RiverPOP: Måle konsentrasjoner av persistente organiske forurensende stoffer og metaller i norske elver

Sammendrag – summary

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 Drammenselva River in 2008. This work focussed on 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 contaminant concentrations while continuous flow centrifugation, time-integrative suspended particulate matter sampling and large volume water sampling were conducted to measure contaminants associated with the particulate phase. Contaminant limits of detection were in the low pg L^{-1} range and agreement between the different methods was observed. Following further improvements, these methods may become a vital part of the RID monitoring programme for the evaluation of riverine fluxes of contaminants.

4 emneord RID program, konsentrasjon av metaler og POPs, passiv prøvetakene, sedimentfeller	4 subject words RID programme, POP and metal concentrations, passive sampling, suspended particulate matter