



**KLIMA- OG  
FORURENSNINGS-  
DIREKTORATET**

*Statlig program for forurensningsovervåking  
Rapportnr. 1095/2011*

***Tilførselsprogrammet 2010***  
**Passive air and water sampling at Andøya, Bjørnøya  
and Jan Mayen, 2009-2010**

TA  
2808  
2011

*Tilførselsprogrammet utføres av:*



Statens strålevern  
Norwegian Radiation Protection Authority



# Norwegian Institute for Water Research

– an institute in the Environmental Research Alliance of Norway

# REPORT

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Tilførselsprogrammet: 2010 Passive air and water sampling at Andøya, Bjørnøya and Jan Mayen, 2009-2010	Report No. 6188-2011	Date 24. mai 2011
	Project No. O-11309	Pages      Price 53
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	Geographical area Norwegian Sea	Printed NIVA

Client(s) Klima- og forurensningsdirektoratet (Klif)	Client ref. TA-2808/2011
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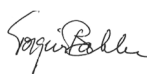
**Abstract**

As part of the Climate and Pollution Agency (Klif) monitoring programme on fluxes of contaminants in the Barents Sea, Norwegian Sea and North Sea, passive sampling was undertaken at Andøya, Bjørnøya and Jan Mayen to measure levels of polycyclic aromatic hydrocarbons (PAHs), polychlorinated biphenyls (PCBs), organochlorines (OCs) and polybrominated diphenylethers (PBDEs) in air and water. Semipermeable membrane devices and silicone strips were deployed in water for periods of 10-12 months. PAH levels in water were low, but mostly quantifiable. PCB levels were mostly below limits of detection (LOD), the latter being in the low picogram/litre range. LODs were adequate for pentachlorobenzene and hexachlorobenzene, while concentrations of hexachlorocyclohexane isomers (-HCH and -HCH) and *p,p'*-DDE were closer to the LOD. PBDE-47 and PBDE-99 were consistently detected. For certain compounds, it was possible to compare dissolved water concentrations to levels in the sediment and in cod liver. Results from polyurethane foam samplers (PUFs) deployed in the air are broadly consistent with results from past findings and active air samplers, yet also revealed difficulties when applying passive sampling methods in the harsh Arctic climatic conditions. Contaminant levels in air were successfully measured at the three sites using PUF air samplers. Some recommendations regarding further work are provided.

4 keywords, Norwegian	4 keywords, English
1. Passive prøvetaking	1. Passive sampling
2. Arktisk overvåking	2. Arctic monitoring
3. Luft og vann prøvetaking	3. Air and water sampling
4. Organiske miljøgifter	4. Organic pollutants



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Tilførselsprogrammet 2010:

**Passive air and water sampling at Andøya, Bjørnøya  
and Jan Mayen**

Data from 2009-2010

## **Foreword**

Klima- og forurensningsdirektoratet (Klif) har etablert et langsiktig program for overvåking av tilførsler av miljøfarlige stoffer til forvaltningsplanområdene Barentshavet, Norskehavet og Nordsjøen (Tilførselsprogrammet). Tilførslene fordeles mellom bidrag fra 8 kilder og til 12 regioner. I 2009 ble programmet utvidet til å omfatte overvåking som primært skal dekke behov i forvaltningsplanene, og utfylle og supplere eksisterende programmer på nasjonalt og internasjonalt nivå.

Dette prosjektet er utført av Norsk institutt for vannforskning (NIVA) i partnerskap med Havforskningsinstituttet (IMR), Nasjonalt institutt for ernærings- og sjømatforskning (NIFES), Norsk institutt for luftforskning (NILU), Statens strålevern (NRPA) og Bjerknes Centre for Climate Research (BCCR) ved Klif kontrakt nr. 5011020. Denne rapporten gjelder undersøkelser ved hjelp av passive prøvetakere i 2010 utført av NIVA og NILU. Tre andre rapporter fremstiller: undersøkelser av miljøgifter og radionuklider i Nordsjøen i 2010 (utføres av NIVA, IMR, NIFES, NILU og NRPA), undersøkelser av havforsuring (utføres av NIVA, IMR og BCCR) og undersøkelser fra faste værstasjon på Andøya i 2010 (utføres av NILU).

Vi vil takke senioringeniør Christine Daae Olseng og sjefsingeniør Gunnar Skotte, begge fra Klif, for god oppfølging og støtte under gjennomføringen av prosjektet.

Takk rettes også til staben på meteorologiske stasjonene på Bjørnøya og Jan Mayen, og personalet ved rakettutskytningsområdet på Andøya (ALOMAR), og til mannskapet fra Kystvakten for feltarbeid.

SPMD- og silikonstrimmel-prøvetakere, samt ekstraksjon og analyse av disse ble gjennomført av NIVA. PUF passive-prøvetakere, samt ekstraksjon og analyse av disse ble gjennomført av NILU. Forsker Guttorm Christensen (Akvaplan-niva) sto for hoveddel av organisering og gjennomføring av feltarbeidet.

forsker Ian J. Allan (NIVA) har vært delprosjektleder og vært hovedansvarlig for utforming av rapporten med betydelig bidrag fra forsker Wenche Aas (NILU). Forsker Norman W. Green (NIVA), forsker Kine Bæk (NIVA), forsker Guttorm Christensen (Akvaplan-niva) og forsker Knut Breivik (NILU) har også arbeidet med rapporten.

Forsker Norman Green har vært leder for hele prosjektet. Forskningsleder Torgeir Bakke har vært faglig kvalitetssikrer for rapporten.

Etter avtale med Klif har denne rapporten egen mal og er skrevet på engelsk .



Norman W. Green  
Oslo, 20. mai 2011



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## Summary

The Climate and Pollution Agency (Klif) has established a long-term monitoring programme to assess fluxes of contaminants in the Barents Sea, Norwegian Sea and North Sea. This includes the measurement of trace levels of organic contaminants in air, water, sediment and biota at Andøya on the Norwegian coast, Bjørnøya and Jan Mayen. These three sites were selected to obtain adequate spatial coverage of large bodies of water and because it was possible to deploy passive sampling devices both in air and water at the sites. The sites provide good coverage for the measurement of contaminant levels in water masses moving from the Atlantic ocean towards Norway's coastal areas or those from the Arctic. In addition sampling at Andøya provides information on Norwegian currents.

For air and water monitoring, passive sampling was selected for its ability to provide low limits of detections and time-integrative information on levels in these compartments. The aim of this work was to establish a long-term programme for the measurement of levels and temporal trends in polycyclic aromatic hydrocarbons (PAHs), polychlorinated biphenyls (PCBs), organochlorines (OCs) and polybrominated diphenylethers (PBDEs) concentrations at the three selected sites.

For the monitoring of contaminants dissolved in water, two types of samplers made of different polymers were selected for this work. Semipermeable membrane devices (SPMDs) and silicone strips were deployed for periods of 10-12 months at each of the three sites. Relatively novel data were obtained from the Andøya and Bjørnøya while samplers exposed at Jan Mayen were lost due to sea conditions. SPMDs and silicone strips were also exposed in the air at these three sites (data analysis and interpretation is forthcoming). The relatively lengthy deployments for samplers exposed at Andøya and Bjørnøya ensured better limits of detection. The longer deployment at Bjørnøya enabled the quantification of a large number of compounds (e.g. for PAHs) than for the shorter exposure. Despite the lengthy deployments, it was possible to use the dissipation of performance reference compounds to assess analyte sampling rates, and dissolved concentrations for compounds of interest.

PAH concentrations in water were low but mostly quantifiable. PCB concentrations were mostly below limits of detection, despite those being in the low picogram/litre ( $\text{pg L}^{-1}$ ) range. Limits of detection were adequate for pentachlorobenzene and hexachlorobenzene, while concentrations of hexachlorocyclohexane isomers ( $\alpha$ -HCH and  $\gamma$ -HCH) and *p,p'*-DDE (a metabolite of DDT) were close to limits of detection. Two PBDE congeners, the tetrabromodiphenylether PBDE-47 and the pentabromodiphenylether PBDE-99 were consistently detected. Concentrations generally appear to be of the correct magnitude. Data obtained with the two types of samplers were consistent.

For certain compounds, it was possible to compare dissolved water concentrations with those measured in the whole sediment and accumulated in cod liver. Organic carbon-normalised bottom sediment-water distribution coefficients were generally substantially higher than expected based on literature information implying stronger binding of the compounds to sediment particles. Bioaccumulation factors based on contaminant concentrations in cod liver ( $\log\text{BAF}$ ) were generally close to compound's  $\log K_{ow}$  values. Forthcoming results include a comparison of contaminant concentrations in air and water on the basis of SPMD and silicone samplers.

Polyurethane foam samplers (PUFs) were deployed in the air the same three sites. The results obtained on the basis of these passive air samplers are broadly consistent with results from past findings and active air samplers (at other Arctic monitoring sites), yet also revealed difficulties when applying this method at Arctic sites, which are mainly attributed to the relatively harsh climatic conditions (colder temperatures and elevated wind speeds). Thus, the results presented are only expected to represent the "true" air concentrations within a factor of ~2-3. Levels of persistent organic pollutants (POPs) in air have successfully been measured at three sites using PUF passive air samplers. Air concentrations

have been back-calculated using depuration compounds, providing estimates of *in situ* uptake rates. The windy conditions often experienced at these Arctic sites lead to uncertainties in back-calculated air concentrations. The uncertainty in the passive air-sampling (PAS) method (i.e. a factor 2-3) combined with the limited number of stations makes it difficult to infer something about spatial patterns in air on the basis of the existing dataset.

As a conclusion, useful and novel data was obtained from samplers deployed in the air and water at Andøya and Bjørnøya while samplers exposed at sea at Jan Mayen were lost due to the sea conditions. This work has shown that passive sampling in air and water has the potential to provide useful data on contaminant levels at sites where it is generally difficult to undertake any other types of measurements reliably. Importantly passive samplers were able to provide time-integrated data on contaminant levels in air and water masses. Some improvements of a methodological nature could be made to lower limits of detection or to obtain more detailed information on seasonal variations.

Based on results presented here, some recommendations and proposals for future work are also provided in this report. Recommendations regarding the methodology for passive sampling in water include the evaluation of the constancy of sampling rates for samplers exposed for as long as a year, knowledge of the effect of water temperature and salinity on sampler-water contaminant partition coefficient. For passive air sampling more information on seasonal variations could be obtained from shorter deployments. The implementation of similar types of samplers in air and water would help to estimate air-water concentration gradients and fluxes between these compartments. The list of contaminants that can be measured by passive sampling could also be widened, however this may require the use of other types of samplers for air and water. The spatial coverage could be increased to include an increasing number of sampling sites on the Norwegian coast.





## Utvidet sammendrag

### Mål og organisering av passiv prøvetakingsstudie

Klima- og forurensningsdirektoratet (Klif) har etablert et langsiktig overvåkingsprogram for tilførsel av miljøgifter i Barentshavet, Norskehavet og Nordsjøen. Dette inkluderer måling av organiske miljøgifter i luft, vann, sediment og biota på Andøya, Bjørnøya og Jan Mayen (**Figur 1**). Passiv prøvetaking ble valgt for luft- og vannovervåking på grunn av lave deteksjonsgrenser og langtidsinformasjon om nivåer i disse mediene. Målet med dette arbeidet var å etablere et langsiktig program for måling av nivåer og tidsmessige trender av polisykliske aromatiske hydrokarboner (PAH), polyklorerte bifenyler (PCB), klorerte hydrokarboner (OC) og polybromerte difenyletere (PBDE) ved de tre utvalgte lokalitetene.

To ulike typer av prøvetakere ble valgt for å overvåke oppløste miljøgifter i vann i denne undersøkelsen. Semipermeable membraner (Semipermeable membran devices - SPMD) og silikonstrimler var utplassert i perioder på 10-12 måneder på hvert av de tre stedene. For luftprøvetaking var eksponeringstiden kortere, og målingene ble foretatt med hjelp av skiver av polyuretan.



**Figur 1.** Kart som viser utvalgte områder for passiv prøvetaking (røde prikker). Koordinater for luftprøvetaking på Andøya, Bjørnøya og Jan Mayen var henholdsvis  $N69^{\circ}09.510'$   $E15^{\circ}59.740'$ ,  $N74^{\circ}30.210'$   $E18^{\circ}59.570'$  and  $N70^{\circ}58.700'$   $W8^{\circ}29.500'$ .

### Metodikk

Passive prøvetakere er polymerer som gjennom diffusjon kan akkumulere kjemikalier oppløst i vann under eksponering *in situ*. Med riktige kalibreringsmetoder (dvs. ved bruk av referanseforbindelser, PRCs), er det mulig å estimere opptakshastigheten og beregne gjennomsnittskonsentrasjoner av kjemikalier oppløst i vann under eksponeringsperioden. Semipermeable membraner (SPMDs) består av en absorbent (triolin) som eksponeres for vannet gjennom en tynn membran, og har vært brukt for overvåking av upolare miljøgifter i vann de to siste tiårene. Silikonstrimler preparert av NIVA ble også brukt til overvåking av upolare organiske forbindelser i vann. Prøvetakene hadde omtrent likt overflateareal som SPMDs, men et større volum som følge av tykkelsen av silikonstrimmelen. Det er

forventet at silikonstrimler kan være bedre tilpasset for prøvetaking under de kalde forholdene som kan forekomme på de utvalgte prøvetakingsstasjonene. Begge typer prøvetakere bruker PRCs for beregning av prøvetakingsfrekvens.

Tilsvarende som for vann, har passiv prøvetaking av organiske miljøgifter i luft blitt stadig mer brukt det siste tiåret. Passive prøvetakere bestående av polyuretanskum-skiver (PUF-luftprøvetaker) kan også integrere informasjon over perioder på noen uker opp til et par måneder.

Prøvetakere ble utplassert i vannet i egnede SPMD-bur fastmontert på rigger på hver lokalitet for perioder på 263-362 dager. For luftprøvetakingen varierte eksponeringstiden mellom 89-171 dager. "UFO"-prøvetakere ble brukt for beskyttelse av PUF-skivene.

Luft- og vannprøvene ble analysert for PAH, PCB, OC og PBDE ved NILU og NIVA. I tillegg ble klordaner målt i luftprøvene. Noen prøvetakere ekstra (SPMDs og silikonstrimler) ble utplassert i luft så vel som i vann, men data for disse vil bli rapportert senere. Alle prøveekstrakter ble også analysert for referanseforbindelser for å muliggjøre beregning av opptakshastighet av miljøgifter i prøvene.

PRC-basert opptakshastighet for passive prøvetakere utplassert i vann varierte mellom 1.5 - 2.7 Lday<sup>-1</sup> for stoffer av interesse for Andøya og Bjørnøya.

### Forurensningskonsentrasjoner i vann

Utvalgte eksempler på data er presentert i *Tabell 1* og *Tabell 2*. Alle analyseresultater er presentert i hovedrapporten. *Tabell 1* og *Tabell 2* presenterer estimerte konsentrasjoner av oppløste miljøgifter i vann, som anvendes til å estimere fordelingskoeffisienter mellom sediment og vann og bioakkumuleringsfaktorer basert på nivåer av miljøgifter målt i torskelever for Andøya sammenlignet med Bjørnøya. Disse er gitt for benzo(a)pyren, heksaklorbenzen (HCB), HCH isomere og *p, p'*-DDE. Repliserbarheten vist ved parallelle prøvetakere er god.

De fleste PAH-forbindelsene var over deteksjonsgrensen, og data fra de to ulike prøvetakene var i de fleste tilfeller samsvarende og forskjeller i konsentrasjoner er godt innenfor en faktor 2. Standardavvik basert på replikater ligger innenfor et meget akseptabelt område (<20 %), særlig når man vurderer den lange eksponeringstiden. For de fleste PAH med  $\log K_{ow} > 5.5$  var oppløste konsentrasjoner under 1 ng L<sup>-1</sup>.

Oppløste konsentrasjoner av  $\alpha$ - og  $\gamma$ -HCH, *p, p'*-DDE og HCB ble målt på Andøya og Bjørnøya. HCB ble påvist både med silikonstrimler og SPMDs, og sillet i estimat av vannkonsentrasjon ligger godt innenfor en faktor 2. Deteksjon av  $\alpha$ - og  $\gamma$ -HCH var mulig med silikonstrimler, mest sannsynlig på grunn av deres større volum, som resulterte i lavere deteksjonsgrense for forbindelser som relativt raskt kommer i likevekt. Konsentrasjonene for disse HCH-isomerene var under 1 ng L<sup>-1</sup>. Bare *p, p'*-DDE ble funnet i nivåer nær deteksjonsgrensen i SPMDs. De fleste PCB-kongenerne var under deteksjonsgrensen som lå i det lave pg L<sup>-1</sup>-området. For  $\alpha$ - og  $\gamma$ -HCH isomerer, støtter observerte konsentrasjoner ved Bjørnøya dagens teori om at det skjer en destillasjon av  $\gamma$ -isomerer under lufttransport over Atlanterhavet (havet fungerer som en resipient). Denne prosessen øker det relative nivået av  $\alpha$ -isomerer i luften i Arktis, og resulterer i en økning relativt til konsentrasjoner av  $\alpha$ -HCH i arktisk vann. Foto-isomeriseringsprosesser som konverterer  $\gamma$ -HCH til  $\alpha$ -HCH kan også forklare de relative konsentrasjonene av de to isomerene.

To PBDE-forbindelser, tetrabromodiphenylether PBDE-47 og pentabromodiphenylether PBDE-99, er gjennomgående detektert i silikonstrimler og SPMDs på alle lokaliteter. På Andøya ble også PBDE-28 funnet i konsentrasjoner over deteksjonsgrensen i SPMDs. Konsentrasjonene av PBDE-47 og PBDE-99 målt med silikonstrimler og SPMDs samsvarte meget godt, mens forskjellene mellom de to typene

av prøvetakere var mer tydelig for dataene fra Bjørnøya. De lave temperaturene i vannet på Bjørnøya kan ha påvirket de to ulike typer prøvetakere forskjellig. Konsentrasjonene ligger på lave pg  $L^{-1}$  nivå. En estimert konsentrasjon på  $0.40 \text{ pg } L^{-1}$  PBDE-100 ble også funnet etter den lengste eksponeringstiden med SPMDs.

Som en del av prosjektet ble også konsentrasjoner av ulike forurensninger målt i sedimenter (øverste 2 cm) og i torskelever (*Gadus morhua*) ved stasjoner på Andøya og Bjørnøya. Det var dermed mulig å beregne teoretiske distribusjonskoeffisienter fra konsentrasjoner av miljøgifter akkumulert i bunnsedimentene ( $C_{sed}$ ), andel av organisk karbon i sedimentet ( $f_{oc}$ ) og miljøgifter oppløst i vannsøylen ( $C_w$ ). Log  $K_{oc}$  verdier for PAH befinner seg innenfor området 6.44 til 8.57, og synes å øke med forbindelsenes hydrofobisitet. Kun små forskjeller i nivåene kan observeres på de to lokalitetene. For PCB, OCs og PBDE, varierer log  $K_{oc}$  fra 3.33 for  $\alpha$ -HCH til 7.11 for PBDE-209. Log $K_{oc}$  for  $\gamma$ -HCH ser ut til å være litt høyere enn for  $\alpha$ -isomeren, og dette stemmer godt overens med deres respektive log  $K_{ow}$  verdier.

Bioakkumuleringsfaktorer (BAF) for forbindelser (noen PCB, OCs og PBDE) målt i torskelever fra Andøya og Bjørnøya ser ut til å være i samsvar med log  $K_{ow}$  for de respektive forbindelsene.

**Tabell 1.** Estimering av oppløst konsentrasjon i vann ( $C_w$ ), sediment-vann distribusjonskoeffisient (normalisert organisk karbon  $K_{oc}$ ) og bioakkumuleringsfaktor (BAF) basert på konsentrasjoner målt i torskelever for utvalgte miljøgifter for Andøya.

Analytt	Log $K_{ow}$	$C_w^a$ (ng $L^{-1}$ )	Log $K_{oc}^b$ (L $kg^{-1}$ OC)	BAF <sup>c</sup> (L $kg^{-1}$ lipid)
Benzo[a]pyren	6.05	0.016 (SPMD)	7.97	
HCB	5.50	0.029 (SPMD)	4.76	5.48
A-HCH	3.81	0.47 (SIL)	3.33	3.60
$\Gamma$ -HCH	4.14	0.37 (SIL)	6.22	7.07
<i>p,p'</i> -DDE	6.29	0.0042 (SPMD)	-	

<sup>a</sup> oppløst konsentrasjon i vann  
<sup>b</sup> normalisert organisk karbon sediment-vann distribusjonskoeffisient  
<sup>c</sup> bioakkumuleringsfaktor (torskelever) normalisert til lipidvekt innhold  
\* SIL og SPMD indikerer om data er fra silikonstrimler eller SPMD

**Tabell 2.** Estimering av oppløst konsentrasjon i vann ( $C_w$ ), sediment-vann distribusjonskoeffisient (normalisert organisk karbon  $K_{oc}$ ) og bioakkumuleringsfaktor (BAF) basert på konsentrasjoner målt i torskelever for utvalgte miljøgifter for Bjørnøya (lengste eksponeringsperiode er 363 dager).

Analytt	Log $K_{ow}$	$C_w^a$ (ng $L^{-1}$ )	Log $K_{oc}^b$ (L $kg^{-1}$ OC)	BAF <sup>c</sup> (L $kg^{-1}$ lipid)
Benzo[a]pyren	6.05	<0.010 (SPMD)	-	-
HCB	5.50	0.048 (SPMD)	5.52	5.65
A-HCH	3.81	0.83 (SIL)	3.52	3.59
$\Gamma$ -HCH	4.14	0.39 (SIL)	4.02	3.85
<i>p,p'</i> -DDE	6.29	0.0023 (SPMD)	-	-

<sup>a</sup> oppløst konsentrasjon i vann  
<sup>b</sup> normalisert organisk karbon sediment-vann distribusjonskoeffisient  
<sup>c</sup> bioakkumuleringsfaktor (torskelever) normalisert til lipidvekt innhold  
\* SIL og SPMD indikerer om data er fra silikonstrimler eller SPMD

## Sammenligning med EUs Vanddirektiv for miljøkvalitetsstandarder

Gjennom Vanddirektivet (*Water Framework Directive legislation* (2000/60/EC)), har den europeiske unionen etablert miljøkvalitetsstandarder (*Environmental Quality Standards* (AA-EQS)) for prioriterte stoffer (2008/105/EC) gjeldende for ferskvann og kystnære farvann. Forutsatt at disse EQS-konsentrasjonene kan brukes i områder rundt Jan Mayen og Bjørnøya, gir de et grunnlag som referanseverdier for å kunne etablere en god vannkvalitetsstatus. Man må imidlertid huske på at konsentrasjonene målt med passive prøvetakere er for oppløste miljøgifter, mens AA-EQS verdier refererer til ufiltrerte vannprøver. I gjennomsnitt er konsentrasjoner fra passiv prøvetaking for Andøya og Bjørnøya >1000 ganger lavere enn AA-EQS verdier for antracen, benzo(a)pyren og *p, p'*-DDT. Konsentrasjonene av fluoranten, heksaklorbenzen, pentaklorbenzen og benzo(b+k)fluoranten er mellom 100 og 1000 ganger lavere enn AA-EQS verdier. I gjennomsnitt er summen av konsentrasjoner av benzo(ghi)perylene, indeno(1,2,3-cd)pyren, og heksaklorsykloheksan ca. 50 ganger lavere enn EQS verdier. De høyeste PBDE-konsentrasjonene ble målt for PBDE-47 og PBDE-99 med konsentrasjoner mellom 2 og 8 pg L<sup>-1</sup> som er nær en faktor 30 lavere enn EQS.

### Konsentrasjoner av forurensninger i luften

Gjennomsnitt for bestemte perioder ble beregnet for hele prøvetakingsperioden for mer sammenlignbarhet med målinger i havet (PAH og PCB/OCs data er gitt i **Tabell 3** og **Tabell 4**). Gjennomsnittet var vektet med antall dager for hver prøvetakingsperiode og data under deteksjonsgrensen ble satt til halve deteksjonsgrensen. Den gjennomsnittlige konsentrasjonen av åtte forskjellige PAH-forbindelser var ganske lik (1-2 ng m<sup>-3</sup>) for alle lokaliteter med en liten reduksjon fra avstand til fastlandet og til de største utslippskilder, men forskjellen er for liten til å være signifikant. Nivåene er sammenlignbare med det som er rapportert tidligere. De vanligste PAH-forbindelsene inkluderer fenantren og fluoren, og bidraget fra tyngre PAH med høyere affinitet for partikulært material er mye lavere. Konsentrasjonen av PCB-forbindelser er noe høyere på Andøya sammenlignet med de to andre stedene, og forskjellen er relativt stor for tyngre PCB. Dette er et generelt mønster på grunn av begrenset potensial for atmosfærisk transport av tyngre PCB med økende avstand fra kilder. Konsentrasjonen av HCB er derimot høyest ved Jan Mayen og lavest på Andøya, tilsvarende er også observert for pentaklorbenzen (PeCB). Disse er også blant de mest flyktige stoffene som er blitt undersøkt og som kan ha nådd likevekt under prøvetakingsperiodene. Kaldere lufttemperaturer som typisk også er korrelert med vindhastigheter og forventet i de nordligste områdene, vil fremme forbedret partisjon og opptak fra gassfase til PUF. Dette fører til at større mengder stoffer bindes til PUF på den nordligste stasjonen, og kan dermed bidra til å forklare de høyere konsentrasjoner på de nordligste områdene. Dette illustrerer også tilfeldigvis noen av begrensningene til *passive air-sampling* (PAS)-metoden når det brukes i kalde og vindfulle områder i Arktis. Nivåene av HCB er også signifikant høyere enn hva vi har sett i den gjennomsnittlige konsentrasjonen av HCB i den passive kampanjen i Europa i 2006 (49 ± 18 pg m<sup>-3</sup>). For aktive prøver er HCB-konsentrasjonene ganske like sammenlignet med steder i Sør-Norge (Birkenes) og Zeppelin (Svalbard) med målte nivåer mellom 65- og 85 pg m<sup>-3</sup> de siste årene. For klordaner er nivåene mellom lokalitetene sammenlignbare, og dessuten er nivået av enkelte klordaner samt summen av de fire utvalgte forbindelsene veldig lik det gjennomsnittlige europeiske nivået i luft som ble observert i den passive kampanjen sommeren 2006, dvs. 3.5 ± 2.7 pg m<sup>-3</sup>. Konsentrasjonen av α-HCH er høyere på de to mest arktiske områdene sammenlignet med Andøya. Dette kan reflektere at havet kan fungere som en kilde til α-HCH og/eller økt opptak på grunn av kulde og økte vindhastigheter, men usikkerheten i metoden er for høy til å kunne konkludere dette. Som forventet med redusert mulighet for langtransport på grunn av økt potensiale av utvasking av regn, er nivået av γ-HCH lavere enn α-HCH i disse arktiske strøk. For DDT er den høyeste konsentrasjonen sett på Bjørnøya, og for alle områder er *p, p'*-DDE er den viktigste isomeren. Nivåene er imidlertid høyere enn det som tidligere har blitt observert ved aktiv prøvetaking på Zeppelinstasjonen; 0.43 pg m<sup>-3</sup> i 2009.

**Tabell 3.** Konsentrasjon av PAH målt i luften med PUF plater på Andøya, Bjørnøya og Jan Mayen.

	<b>Andøya</b>	<b>Bjørnøya</b>	<b>Jan Mayen</b>
<b>Sattut</b>	<b>29.11.09</b>	<b>29.12.09</b>	<b>05.01.10</b>
<b>Tatt inn</b>	<b>16.08.10</b>	<b>28.08.10</b>	<b>29.07.10</b>
Fluoren	0.7	0.6	0.7
Fenantren	0.7	0.5	0.3
Antracen	0.01	0.005	0.002
Fluoranthen	0.2	0.2	0.1
Benz[a]antracen	0.01	0.003	0.001
Chrysen	0.02	0.016	0.012
Benzo[a]pyren	0.01	0.001	0.003
Pyren	0.08	0.06	0.03
<b>Sum 8 PAH</b>	<b>1.7</b>	<b>1.3</b>	<b>1.1</b>

**Tabell 4.** Konsentrasjon av PCB og OCs i luften målt med PUF plater på Andøya, Bjørnøya og Jan Mayen.

	<b>Andøya</b>	<b>Bjørnøya</b>	<b>Jan Mayen</b>
<b>Sattut</b>	<b>29.11.2009</b>	<b>29.12.2009</b>	<b>05.01.2010</b>
<b>Tatt inn</b>	<b>16.08.2010</b>	<b>28.08.2010</b>	<b>29.07.2010</b>
<b>PCB-28</b>	3.5	2.1	1.7
<b>PCB-52</b>	2.5	2.3	2.0
<b>PCB-101</b>	2.5	1.4	1.1
<b>PCB-118</b>	0.6	0.5	0.3
<b>PCB-138</b>	1.7	0.5	0.4
<b>PCB-153</b>	2.3	0.8	0.6
<b>PCB-180</b>	0.8	0.2	0.1
<b>Sum 7 PCB</b>	<b>14</b>	<b>8</b>	<b>6</b>
<b>HCB</b>	66	107.	129
<b>PeCB</b>	9	12	16
<b>trans-Chlordane</b>	0.6	1.0	1.0
<b>cis-Chlordane</b>	1.4	2.4	2.2
<b>trans-Nonachlor</b>	1.2	2.0	19
<b>cis-Nonachlor</b>	0.1	0.1	0.1
<b>Sum 4 chlordanes</b>	<b>3.3</b>	<b>5.6</b>	<b>5.2</b>
$\alpha$ -HCH	12	21	19
$\gamma$ -HCH	2.9	3.1	2.6
p,p'-DDE	1.8	4.3	2.2
p,p'-DDD	0.06	0.07	0.2
o,p'-DDT	0.5	0.9	07
p,p'-DDT	0.3	0.6	0.3
<b>Sum 4 DDTs</b>	<b>2.7</b>	<b>5.8</b>	<b>3.4</b>

## Sammenligning av konsentrasjoner i luft og vann

Overføring av miljøgifter fra luft til sjøvann gjennom diffusjon er en sentral transportvei for hvordan disse fremmedstoffer kommer til det marine miljøet. Det er noen grunnleggende utfordringer involvert i noen estimater av luft-vann utveksling og spesielt under forhold når luft og sjøvann er i nær likevekt og/eller når forbindelser av interesse er nær deteksjonsgrensene. Likevel, fordi passive prøvetakere i luft og sjøvann har vært samlokalisert på både Bjørnøya og Andøya, er det mulig å benytte anledningen til å vurdere retning av flukser for utvalgte forbindelser. Dette kan hjelpe til med å påpeke videre forskningsbehov. For disse beregningene på fysisk-kjemiske egenskaper og temperaturavhengighet, ble informasjonen brukt til å beregne  $F_{\text{luft}} / F_{\text{vann}}$  forholdstall for HCH isomere og HCB på Andøya og Bjørnøya. Disse forholdstall er generelt under 1, som indikerer en luft-til-vann-flux. Likevel er intervallet for disse verdiene store. En ytterligere skjevhet med en faktor på to kan forventes for passiv prøvetakings-data i vann.

## Konklusjoner for overvåking i vann

Passive prøvetakere (semipermeable membranheter og silikonstrimler) ble utplassert på tre steder, hhv. Andøya, Bjørnøya og Jan Mayen. Nye og nyttige data er innhentet fra de to første stedene, mens prøvetakere eksponert på sistnevnte gikk tapt. SPMDs og silikonstrimler ble også eksponert i luft på disse tre stedene (dataanalyse og tolkning kommer). Den relativt lange eksponeringen av prøvetakene på Andøya og Bjørnøya medførte lavere deteksjonsgrenser. Den lange eksponeringstiden på Bjørnøya medførte at et stort antall forbindelser ble kvantifisert (for eksempel for PAH). For visse forbindelser var det mulig å sammenligne konsentrasjoner i vann med de som ble målt i sedimentet og fiskelever (torsk).

Hovedkonklusjoner:

- Bruk av referanseforbindelser tillot kvantifisering av forurensningens utvekslingskinetikk mellom vann og prøvetakere, og dermed kunne opptakraten for hele eksponeringsperioden beregnes.
- Deteksjonsgrensen for PAH-forbindelser etter 12 måneders eksponering er akseptabel.
- PCB-konsentrasjoner i vann er svært lave, og nær eller under deteksjonsgrensen ved både Andøya og Bjørnøya. Deteksjonsgrensene betraktes i seg selv som lave.
- Deteksjonsgrensene av PeCB og HCB er akseptable.
- Deteksjonsgrensene for *p, p'*-DDE og HCH isomerene er i samme området som for de oppmålte konsentrasjonene. Silikonstrimler ser ut til å absorbere en større mengde HCH-isomerer enn SPMDs. Dette kan forbedres ytterligere ved å optimalisere prøvetakerens egenskaper.
- PBDE-47 og PBDE-99 er gjennomgående funnet over deteksjonsgrensene.
- Prøvetakingskvaliteten med silikonstrimler og SPMDs er lik. Det er imidlertid mulig at avvik i data innhentet med de to ulike prøvetakene skyldes ulik effektivitet ved lav temperatur.
- Om man ikke endrer designet på prøvetakerne betydelig, burde eksponeringstiden være 12 måneder ved bruk i vann. Alternativt kan eksponering foretas ved hjelp av en annen type av bur for å muliggjøre høyere vannturbulens nær prøvetakerens overflate og dermed høyere opptakshastighet (og lavere deteksjonsgrense).
- Eksponering i luft med tidsintegreerte absorpsjonsprøvetakere (som SPMDs og silikonstrimler) påviste forekomst av enkelte miljøgifter (kommende resultater).
- I de fleste tilfeller er de estimerte miljøgiftkonsentrasjoner i vann godt under miljøkvalitetsstandarder satt av EUs rammedirektiv for vann (WFD).

- Passive prøvetakere kan gi informasjon om miljøgifter på steder hvor det generelt er vanskelig å få tatt prøver av biota. I tillegg er de svært egnet til vurdering av langsiktige trender av konsentrasjoner.
- Grove estimater av luft-vann-utveksling ble gjort ut fra luft- og vannkonsentrasjoner, men disse må brukes med forsiktighet, ettersom både luft- og vanndata er gjenstand for usikkerhet.

### **Konklusjoner fra passiv luftprøvetaking**

Resultatene innhentet fra passiv prøvetaking i luft er i samsvar med resultater fra tidligere funn og aktive luftprøvetakere, men avslørte også vanskeligheter når denne metoden brukes i arktiske strøk, som i hovedsak tilskrives de klimatiske forholdene (lavere temperaturer og høy vindhastighet). Dermed er resultatene som presenteres bare forventet å representere den "konkrete" luftkonsentrasjonen innenfor en faktor av ~ 2-3. Dette må tas i betraktning når man tolker resultatene, og dersom disse dataene skal brukes til å diskutere potensiell likevektstatus og fluks mellom luft og overflate sjøvann.

Hovedkonklusjoner:

- Med hjelp av passive luftprøvetakere (PUFs) har nivåer av POPs i luft blitt målt ved tre steder (Jan Mayen, Bjørnøya og Andøya) for første gang.
- Det totale luftvolumet som blir samlet av prøvetakeren kunne anslås ved å måle avdampning av stoffer som er tilsatt prøvetakeren før start av prøvetaking (depuration compounds). Dette gjør at man kan beregne gjennomsnittlige luftkonsentrasjoner for eksponeringsperioden.
- De vindfulle forholdene som ofte oppleves i disse arktiske områdene fører til usikkerhet i beregnede luftkonsentrasjoner.
- Usikkerheten i PAS-metoden (dvs. en faktor 2-3) kombinert med begrenset antall stasjoner (3) gjør det vanskelig å si noe sikkert om trender og miljøgifter i luft med utgangspunkt i foreliggende datasett.

### **Anbefalinger**

- Metoder for passive prøvetaking i vann bør omfatte en vurdering av opptakrater for prøvetakere som har blitt satt ut over lengre tid og effekt av vanntemperatur og saltholdighet på fordelingskoeffisienten mellom prøvetaker og vann.
- For passive prøvetaking i luft kan kortere eksponering flere ganger over året øke forståelse av sesongmessige forskjeller.
- Bruk av mer like prøvetakere i luft og i vann kan bidra til bedre forståelse av gradienter og flukser mellom disse to mediene.
- Det bør vurderes å utvide undersøkelsen til å omfatte flere miljøgifter, selv om dette kan kreve bruk av andre typer prøvetakere.
- Undersøkelsen kunne med fordel ha omfattet flere stasjoner langs kysten.





# 1. Introduction

The Climate and Pollution Agency (Klif) has established the *Tilførselsprogrammet* - a program for calculations of discharges, transport pathways and deposition of environmental hazardous substances in Norwegian marine areas (Green *et al.*, 2010). This includes the measurement of trace levels of organic contaminants in air, water, sediment and biota at Andøya on the Norwegian coast, Bjørnøya and Jan Mayen. While for many classes of contaminants the measurement of concentrations in sediment and biota is relatively straightforward, the measurement of trace levels in air and water require the use of sampling techniques that allow very low limits of detection. Passive sampling (Vrana *et al.*, 2005) was selected because of its potential to achieve these low limits of detection and for its ability to provide time-integrative information on levels in air and water.

The aim of this work was to establish a long-term monitoring programme for the measurement of levels and temporal trends in polycyclic aromatic hydrocarbon (PAHs), polychlorinated biphenyl (PCBs), organochlorine (OCs) and polybrominated diphenylether (PBDEs) concentrations at the three selected sites. In addition, it is hoped that these data can also support concentrations measured in aquatic biota and in bottom sediment, and provide information on fluxes of contaminants between water and air masses. The three sites selected for this study aimed to provide adequate spatial coverage of large water masses and because the deployment of passive sampling devices both in air and water was possible at these sites. They provide good coverage for the measurement of contaminant levels in water masses moving from the Atlantic ocean towards Norway's coastal areas or water masses from the Arctic. In addition sampling at Andøya provides information on Norwegian currents.

## 2. Material and methods

### 2.1 Sampling sites for passive sampling

As part of the *Tilførselsprogrammet* project, three sites for the measurement of trace organic contaminant levels in water and air were selected. These included a site on the Northern coast of Norway (Andøya), a site near Bjørnøya (Bear Island) between continental Norway and the Spitzbergen, and a site further west at Jan Mayen. Coordinates can be found in *Table 1*, while a map and a picture (for Bjørnøya only) showing the sampling sites is given in *Figure 1* and *Figure 2*.

*Table 1. Coordinates of sites for passive sampling at Andøya and Bjørnøya.*

	Andøya	Bjørnøya	Jan Mayen
<b>Water</b>	N69° 15.442' E16° 10.371'	N74° 30.720' E18° 57.970'	N70° 54.300' W8° 37.400'
<b>Air</b>	N69° 09.510' E15° 59.740'	N74° 30.210' E18° 59.570'	N70° 58.700' W8° 29.500'



*Figure 1. Map showing sites selected for passive sampling (red dots)*



**Figure 2.** The southern part of Bjørnøya. The sampling site for marine water samples are close to the north point of the island. Sampling site (N74° 30.720' E18° 57.970'). Photograph by Guttorm N. Christensen.

## 2.2 Exposure periods

Exposure periods for passive samplers deployed in water at Andøya and Bjørnøya are provided in **Table 2**. Samplers were exposed for 291 days at Andøya and for periods of 263 and 362 days at Bjørnøya. No information is provided for sampling at Jan Mayen, since passive samplers were lost at sea.

**Table 2.** Deployment and retrieval dates and periods of exposure for passive samplers deployed in water at Andøya and Bjørnøya.

	Andøya		Bjørnøya	
			Period 1	Period 2
<b>Deployment</b>	29.10.2009		05.12.2009	28.08.2009
<b>Retrieval</b>	16.08.2010		25.08.2010	25.08.2010
<b>Exposure time (d)</b>	291		263	362

Two passive air samplers were deployed in parallel at each site. The sampling periods were supposed to be three months (90 days), but was sometimes exposed longer due to logistical reasons. Some of the samplers were also lost due to heavy wind. A list of the samplers deployed and analysed are given in **Table 3**.

**Table 3.** Deployment and retrieval dates and periods of exposure for passive samplers deployed in air at Andøya, Bjørnøya and Jan Mayen.

sample	Andøya		Bjørnøya			Jan Mayen		
	1	2	1	2	3	1	2	3
<b>Deployment</b>	29.11.2009	26.02.2010	28.08.2009	29.12.2009	14.04.2010	5.10.2009	5.01.2010	8.04.2010
<b>Retrieval</b>	26.02.2010	16.08.2010	29.12.2009	13.04.2010	28.08.2010	5.01.2010	08.04.2010	29.07.2010
<b>nr.days</b>	89	171	123	105	136	92	93	112

## 2.3 Passive samplers for air and water monitoring

### 2.3.1 Semipermeable membrane devices (SPMDs) and silicone strips

Passive samplers are polymeric devices capable of accumulating, by diffusion, chemicals dissolved in water during exposure *in situ* (Vrana *et al.*, 2005). With appropriate calibration methods (i.e. the use of performance reference compounds), it is possible to estimate *in situ* sampling rates (equivalent volumes of water extracted by the sampler per unit of time) and calculate time-weighted average concentrations for chemicals dissolved in water for the period of exposure. Depending on the characteristics of the compounds of interest, environmental conditions during deployment and the exposure time, sampling can be integrative (accumulation is proportional to the concentration in water and exposure time) or can reach equilibrium. Performance reference compounds (PRCs) can be used to estimate sampling rates *in situ* and inform us on the degree of equilibrium reached for the sampling chemicals of interest.

Different types of devices exist. Semipermeable membrane devices (SPMDs) are composed of low density polyethylene tubing filled 1 mL of ultrapure triolein lipids (volume  $\sim$  5 mL and surface area of 460 cm<sup>2</sup>) and have been used for the monitoring of nonpolar non-ionic substances in water for the past two decades. These are purchased from Exposmeter AB (Sweden). Silicone strips were prepared at NIVA following procedures developed previously (Allan *et al.*, 2010). Samplers were of a similar surface area as SPMDs, but with a larger volume as a result of the thickness of the silicone sheets (0.5 mm). It is expected that silicone strips could improve limits of detection for compounds for which sampling reaches equilibrium. In addition, it may be that silicone material may be more adapted to sampling under the cold conditions that can be experienced at sampling sites selected for this work. Both types of samplers use PRCs for the estimation of sampling rates. PRCs are compounds spiked into the samplers during fabrication and that can dissipate during exposure. Dissipation rates can then be used to estimate sampling rates for PRC analogues (in this case PRCs are deuterated PAHs). Models are however needed to predict sampling rates for a wide range of compound hydrophobicity ( $\log K_{ow}$ ) from the relatively narrower range of  $\log K_{ow}$  values of the PRC data (Huckins *et al.*, 2006 Rusina *et al.*, 2010). For SPMDs, the model developed by Huckins *et al.* (Huckins *et al.*, 2006) was used to estimate sampling rates for compounds of interest. For silicone strips, such a model is not applicable and an alternative methodology was used (Rusina *et al.*, 2010). The major difference between these two models is the relative decrease in sampling rates predicted for compounds with high  $\log K_{ow}$  values. A mild decrease in sampling rates is assumed for the model for silicone strips while a significantly steeper decrease in sampling rate is predicted with the “SPMD” model (see Rusina *et al.*, 2010 and Huckins *et al.*, 2006 for further details).

A sampling cage following exposure is shown below (**Figure 3**).



**Figure 3.** The passive sampling cage recovered after exposure at Bjørnøya. The cage was covered with kelp after 263 days in the ocean. Photograph: Guttorm N. Christensen.

### 2.3.2 Polyurethane foam samplers (PUF) for air monitoring

Analogous to water, passive air sampling (PAS) of organic contaminants has become increasingly used over the last decade or so (Harner *et al.*, 2006). Unlike conventional active air samplers, PAS also integrate information over longer time-periods (weeks, months, years). For these reasons, PAS have proven to be particularly suitable for spatial mapping (Jaward *et al.*, 2004; Pozo *et al.*, 2006), although temporal trend studies are emerging as well. In fact, probably the longest time trends derived for POPs in air on the basis of PAS is based on a network of SPMDs deployed along a latitudinal transect from U.K. to northern Norway since 1994 (Chaemfa *et al.*, 2010; Ockenden *et al.*, 1998; Schuster *et al.*, 2011).

Different PAS materials have been tested and described, and some of the most popular and well-studied types are those based on polyurethane foam (Shoeib and Harner, 2002), SPMDs (Ockenden *et al.*, 1998) and XAD resin (Wania *et al.*, 2003). Whereas PUFs are suitable for exposure from a few weeks and up to a few months, SPMDs and XAD are typically deployed in the field for a year or more. Although the sampling designs for these samplers vary, the sampling material used in each sampler is typically shielded in a protective housing to avoid collection of precipitation and particles, limit or avoid photodegradation and to buffer against any wind speed effects on uptake rates. PUF and XAD-based samplers have been the choice of the GAPS study (Global Atmospheric Passive Sampling Network), which includes more than 60 PAS sites across the world (Pozo *et al.*, 2009). PUFs have also been our choice for this work, based on past experience with these samplers (Halse *et al.*, 2011).

In spite of their popularity, there are also some limitations to the use of PAS to be aware of. A fundamental constraint is that they mainly are sorbing the gaseous fractions of POPs. Thus, they are less suitable for POPs that sorb significantly to atmospheric particles (i.e. substances with a high  $K_{OA}$ ). There are also uncertainties associated with back-calculating air concentrations from amounts of chemical sequestered by the sampler following exposure in the field. For these reasons, it is common to refer to air concentrations derived on the basis of PAS as semi-quantitative only. Past evaluations have suggested that PUFs enables estimates of “true” air concentrations within a factor of 2-3 (Gouin *et al.*, 2005; Harner *et al.*, 2006; Klanova *et al.*, 2008). As for the passive water sampler mentioned above, NILU is also using PRCs to back-calculate site-specific (*in situ*) sampling rates as detailed by Halse *et al.* (2011) and references therein. These are non-native or isotopically-labelled compounds representing a wide range in  $K_{OA}$ . Following the GAPS protocol (Pozo *et al.*, 2009), we only used PRCs which experienced a loss of 40% or more to calculate site-specific sampling rates. A detailed account of the PUF method used at NILU is described in (Halse *et al.*, 2011) who studied the spatial variability of selected POPs in European background air across 86 sites in 34 countries.

However, it should be cautioned that the climatic conditions with heavy winds often experienced at these sampling sites in this project are not ideal for these samplers. The standard methodology requires that the samples (discs) are hanging loose with a wire from the top disc so it can move freely in the wind to minimise wind speed effects on uptake rates. However, this is practically impossible at all the sites as heavy winds may destroy the samplers if they are hanging loose. The discs have therefore been mounted in a fixed position on a solid surface with the bottom disc, see illustration in **Figure 4**. This implies that heavy wind may lead to enhanced uptake rates. Particles and gases may then be more directly transported to the PUF with the strong wind and not by diffusion alone. This possibility will be further discussed under the results.

We also note that the deployment periods used in this study are longer than many past studies, which may have lead to equilibrium between air and PUF concentrations for low  $K_{OA}$ -substances.



Figure 4. Passive PUF air samples at Bjørnøya

## 2.4 Analysis for trace organic contaminants

### 2.4.1 Extraction and analyses at NIVA

Silicone strips were prepared at NIVA according to established procedures. AlteSil<sup>®</sup> polydimethylsiloxane sheets were obtained from Altec Ltd (Cornwall, UK). Samplers, 100 cm long and 2.5 cm wide were produced from 0.05-cm thick sheets. Soxhlet extraction using a combination of acetone/hexane (50:50) was conducted to clean the sheets and remove possible silicone oligomers that may interfere with the chromatography. This step was repeated with fresh solvents. Samplers were then left to dry and were rinsed with methanol prior to spiking with PRCs.

Once samplers spiked, these stored in clean tins in the freezer at -20 °C. These result in the reproducible production of samplers with respect of initial PRC concentrations (< 10 % variability in spiking), sampler volume and surface area and blank levels. Silicone strips and SPMDs were extracted according to procedures previously described (Allan *et al.*, 2011). Silicone strips were extracted with methanol. Extracts were reduced and split for further clean-up and analyses for PAH, PCBs/OCs and PBDEs. SPMDs were dialysed with hexane and reduced prior to clean-up and analysis. Clean up prior to analyses for PAHs consisted of gel permeation chromatography (mobile phase of dichloromethane). For PCBs and PBDEs, extracts were cleaned-up with concentrated H<sub>2</sub>SO<sub>4</sub>. Internal standard for the various analyses

All SPMD controls and exposed samplers were cleaned by ultra pure water and wiped with a clean tissue. Samplers were dialysed twice with 100 mL hexane (Rathburn, HPLC Grade, Scotland) for 24 hours and the extracts combined. Extracts were spiked with internal standards for PAHs; naphthalene-d<sub>8</sub>, biphenyl- d<sub>10</sub>, acenaphthylene-d<sub>8</sub>, pyrene-d<sub>10</sub> and perylene-d<sub>12</sub>, (Chiron AS, Norway), PBDEs; BDE -30, -119, -181 and -209<sup>13</sup>C, (Cambridge Isotope Laboratories, Inc, USA) and PCB/OCs; PCB- 29, -53 and -204 (Dr Ehrenstorfer GmbH -Germany). Hexane extracts were reduced under nitrogen (AGA 5.0 Norway) and split into two. The extracts for BDE determination were cleaned up with sulphuric acid (Merck, for analysis 95-97%, USA) before they were partitioned with acetonitrile (Rathburn, HPLC Grade, Scotland) and the acetonitrile portion quantitatively removed and reduced prior to analysis. The second extracts were cleaned up by gel permeation chromatography. The system consists of two serial couplets Envirogel<sup>™</sup> GPC-clean up column, 19x300mm and 19x150mm (Waters, Sweden). This extract was split whereas one extract was reduced under nitrogen before PAH analysis

and the other extracts were cleaned up with sulphuric acid before reduction under nitrogen and PCBs/OCs analysis.

For silicone strips, the same procedure was used as for SPMDs. However, methanol (Rathburn, HPLC grade) was used as solvent instead of hexane. Extracts were spiked with internal standards for PAHs, PCBs/OCs and PBDEs. First the solvent was exchanged from methanol to iso-hexane (Riedel-Detlaën, Pestanal, Germany) before the extracts were split. Extracts for PAH analysis were cleaned as described for SPMDs. The other extract was cleaned up with sulphuric acid before the solvents were exchanged to acetonitrile/water in preparation of HBCD determination

**PAH analysis:** Extracts were analysed using a HP-6890N gas chromatograph (GC) equipped with a HP 5973 Mass Selective Detector (MS) (Agilent Technologies, USA) operated in single ion monitoring mode (SIM) with electron impact ionisation (70 eV). The identification was made by comparing retention times and specific ions for each compound in standard solutions and sample extracts. Quantification was performed with both internal and external standards. Analytes were separated on a 30 m DB-5 column (0.25 mm i.d. and 0.25 µm film) (Agilent Technologies, USA) and with a helium (AGA 6.0 Norway) flow of 1 mL min<sup>-1</sup>. The temperature was held for 2 min at 60 °C before ramping to 250 °C at a rate of 7 °C min<sup>-1</sup>. The final step was an increase to 310 °C at a rate of 15 °C min<sup>-1</sup> (held for 6 min). The injector, transfer line, ion source and quadrupole temperatures were set to 280, 280, 230 and 150 °C, respectively.

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

**PBDE analysis:** Extracts were analysed using a HP-6890 gas chromatograph (GC) equipped with a HP 5973 Mass Selective Detector (MS) (Agilent Technologies, USA) operated in single ion monitoring mode (SIM) with negative chemical ionisation (NCI) and methane as the reagent gas. The identification was made by comparing retention times and characteristic ions (486/488 for BDE-209 and 79/81 for all other analytes) in standard solutions and sample extracts. The quantification was performed with both internal and external standards. Pulsed splitless injection was used to introduce samples onto a 15 m DB-5MS (0.25 mm i.d. and 0.10 µm film) (Agilent Technologies, USA). The temperature was held for 2 min at 120 °C before ramping to 180 °C at a rate of 25 °C min<sup>-1</sup>. The final two steps were increase to 250 °C then to 345 °C at rates of 15 °C and 25 °C min<sup>-1</sup> respectively (held for 5 min). The flow was kept at 1.1 mL min<sup>-1</sup>. The injector, transfer line, ion source and quadrupole temperatures were set to 280, 325, 250 and 150 °C, respectively.

#### 2.4.2 Extraction and analyses at NILU

The PUF discs were pre-cleaned by soxhlet extraction, dried and spiked with PRCs prior deployment, and returned to the laboratory for clean-up and analysis after exposure in the field. A mixture of internal standards was added to the PUFs before Soxhlet extraction and further clean-up. The cleanup procedure involves separation into two extracts, with acid treatment and silica fractionation for analysis of the halogenated compounds, and silica fractionation for the PAH extracts. The extracts were further concentrated by a gentle stream of nitrogen to ~50 µL and added recovery standards as detailed in Halse *et al* (2011). Identification and quantification of individual substances was carried out using a gas chromatograph coupled to a high resolution (PCBs, hexachlorocyclohexane HCH

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isomers, hexachlorobenzene HCB, DDTs) and low resolution (PAHs, chlordanes) mass spectrometer. For these substances, the expected uncertainty associated with the overall chemical analysis alone is expected to be in the range of 20-35%, but will vary for different compounds and substance groups. Further details on the analytical method used are provided in (Halse *et al.*, 2011). PBDEs were also analysed but these measurements lack internal standards and therefore highly uncertain. Furthermore, the estimates indicate that the PBDEs were generally below detection limit. The results are therefore not reported here.

## 3. Results and discussion

### 3.1 Contaminant concentrations in water

#### 3.1.1 Calculation of dissolved concentrations

Significant PRC dissipation was observed for all samplers and this allowed the estimation of sampling rates for PRC analogues. Most useable PRCs for SPMDs were phenanthrene- $d_{10}$  and chrysene- $d_{12}$  (very low amounts of fluorene- $d_{10}$  were left in the samplers after exposure). Median sampling rates calculated from these three PRCs were in the range 2.3-2.7 L d<sup>-1</sup> for the deployment in Andøya and between 1.7 and 2.1 L d<sup>-1</sup> for exposures at Bjørnøya. Sampling rates calculated from these same three PRCs for silicone strips were in the range 2.4-2.7 L d<sup>-1</sup> for the deployment in Andøya and between 1.5 and 1.9 L d<sup>-1</sup> for exposures at Bjørnøya. These are very close and consistent.

Overall, these sampling rates are relatively low and may be the result of the low temperatures experienced during these deployments. It can be assumed that under these conditions, sampling remained integrative for compounds with log  $K_{ow}$  > 6.0. From this data, deployment and sampler specific sampling rates were estimated for all compounds of interest. Some uncertainty is linked to the selection of the model itself but also can be the result of uncertainty of some of the model parameters (e.g. the log  $K_{ow}$  values used for some compounds such as PBDEs).

#### 3.1.2 Polycyclic aromatic hydrocarbons (PAHs)

Estimated dissolved concentrations of PAHs measured at Andøya are presented in **Table 4**. Most PAHs were above limits of detection. No data for naphthalene is presented due to the level of these compounds in trip and preparation controls. Despite the long exposure time, some PAHs such as dibenzo[*a,h*]anthracene remained below limits of detection (with LODs close 10 pg L<sup>-1</sup>). Some difference in concentrations calculated for data from silicone strips and SPMDs can be seen for compounds with low log  $K_{ow}$  while consistent data is obtained for more hydrophobic ones (**Table 4**). Data in most cases are very consistent and differences in concentrations are well within a factor of 2. Standard deviations based on duplicate samplers are in a very acceptable range (< 20 %), particularly when considering the long exposures. For most PAHs with log  $K_{ow}$  > 5.5, dissolved concentrations were below 1 ng L<sup>-1</sup>.

**Table 4.** Dissolved concentrations of PAHs in water measured with silicone strips and SPMDs at Andøya (dissolved concentration in water ( $C_w$ ) in  $\text{ng L}^{-1}$ ; standard deviation (SD) from replicate samplers). Concentrations above detection limit are shaded.

	Silicone strips		SPMDs	
	$C_w$ ( $\text{ng L}^{-1}$ )	SD	$C_w$ ( $\text{ng L}^{-1}$ )	SD
Acenaphthylene	<0.2		<0.07	
Acenaphthene	0.14	0.01	<0.2	
Fluorene	1.4	0.1	0.24	0.01
Dibenzothiophene	0.15	0.02	<0.035	
Phenanthrene	2.3	0.2	0.47	0.01
Anthracene	0.06	0.01	<0.026	
Fluoranthene	1.1	0.1	0.45	0.04
Pyrene	0.25	0.02	0.14	0.01
Benz[a]anthracene	0.056	0.006	0.043	0.002
Chrysene	0.17	0.02	0.14	0.002
Benzo[b+j]fluoranthene	0.20	0.02	0.17	0.01
Benzo[k]fluoranthene	0.05	0.01	0.045	0.003
Benzo[e]pyrene	0.10	0.01	0.079	0.002
Benzo[a]pyrene	0.018	0.002	0.016	0.001
Perylene	<0.008		0.010	0.001
Indeno[1,2,3-cd]pyrene	0.034	0.004	0.033	0.001
Dibenzo[ah]anthracene	<0.009		<0.011	
Benzo[ghi]perylene	0.030	0.003	0.025	0.001

Dissolved PAH concentrations measured at Bjørnøya during Period 1 are given in **Table 5**. When compared with data from Andøya, a higher number of PAHs were below limits of detection for the samplers exposed for the shortest period of time (Period 1). This is partly due to slightly lower sampling rates for samplers deployed at Bjørnøya and perhaps lower concentrations at that site. As for the data from Andøya, concentrations measured with the two types of samplers are consistent for the relatively more hydrophobic PAHs. Some differences can be seen for compounds that are likely to have reached equilibrium (those with lower  $\log K_{ow}$ ), and this could be the result of the uncertainty in the sampler-water partition coefficients ( $K_{sw}$ ) used in the calculation. Since the samplers are made of different materials, it is likely that for compounds under equilibrium, the data obtained with the two types of samplers is representative of different periods of time (depending on the time needed to reach equilibrium).

**Table 5.** Dissolved concentrations of PAHs in water measured with silicone strips and SPMDs at Bjørnøya during Period 1 (concentration in  $\text{ng L}^{-1}$ ; standard deviation (SD) from replicate samplers). Concentrations above detection limit are shaded.

	Silicone strips		SPMDs	
	Cw ( $\text{ng L}^{-1}$ )	SD	Cw ( $\text{ng L}^{-1}$ )	SD
Acenaphthylene	<0.2		<0.1	
Acenaphthene	0.10	0.01	<0.6	
Fluorene	1.8	0.1	<0.2	
Dibenzothiophene	0.24	0.02	<0.04	
Phenanthrene	2.1	0.2	0.081	0.004
Anthracene	0.043	0.004	<0.03	
Fluoranthene	0.95	0.01	0.22	0.01
Pyrene	0.30	0.01	0.10	0.01
Benz[a]anthracene	0.039	0.001	0.024	0.002
Chrysene	0.15	0.01	0.091	0.003
Benzo[b+] <i>]</i> fluoranthene	0.10	0.01	0.064	0.003
Benzo[k]fluoranthene	0.023	0.001	0.017	0.001
Benzo[e]pyrene	0.070	0.001	0.040	0.002
Benzo[a]pyrene	<0.02		<0.02	
Perylene	<0.02		<0.02	
Indeno[1,2,3- <i>cd</i> ]pyrene	<0.02		<0.02	
Dibenzo[ <i>ah</i> ]anthracene	<0.02		<0.02	
Benzo[ <i>ghi</i> ]perylene	<0.02		<0.02	

Dissolved PAH concentrations measured with passive samplers deployed during Period 2 are presented in **Table 6**. The longer deployment time allowed the detection of indeno[1,2,3-*cd*]pyrene and benzo[*ghi*]perylene with silicone strips, when these analytes were below limits of detection for samplers from Period 1. As for previous PAH data, concentrations obtained with silicone strips and SPMDs is consistent for analytes with  $\log K_{ow} > 5$ .

**Table 6.** Dissolved concentrations of PAHs in water measured with silicone strips and SPMDs at Bjørnøya during Period 2 (concentration in  $\text{ng L}^{-1}$ ; standard deviation (SD) from replicate samplers). Concentrations above detection limit are shaded.

	Silicone strips		SPMDs	
	Cw ( $\text{ng L}^{-1}$ )	SD	Cw ( $\text{ng L}^{-1}$ )	SD
Acenaphthylene	<0.2		<0.07	
Acenaphthene	<0.09		<0.6	
Fluorene	1.3	0.1	<0.17	
Dibenzothiophene	0.19	0.03	<0.04	
Phenanthrene	1.5	0.2	0.16	0.11
Anthracene	0.053	0.004	<0.027	
Fluoranthene	0.60	0.04	0.25	0.09
Pyrene	0.21	0.02	0.11	0.03
Benz[ <i>a</i> ]anthracene	0.026	0.002	0.020	0.003
Chrysene	0.097	0.008	0.084	0.015
Benzo[ <i>b+</i> ]fluoranthene	0.072	0.004	0.063	0.011
Benzo[ <i>k</i> ]fluoranthene	0.016	0.001	0.016	0.003
Benzo[ <i>e</i> ]pyrene	0.054	0.003	0.043	0.008
Benzo[ <i>a</i> ]pyrene	<0.009		<0.010	
Perylene	<0.009		<0.010	
Indeno[1,2,3- <i>cd</i> ]pyrene	0.010	0.001	<0.011	
Dibenzo[ <i>ah</i> ]anthracene	<0.010		<0.012	
Benzo[ <i>ghi</i> ]perylene	0.015	0.001	0.011	

### 3.1.3 Polychlorinated biphenyls (PCBs) and other organochlorines (OCs)

Dissolved concentrations of  $\alpha$ - and  $\gamma$ -HCH,  $p,p'$ -DDE,  $p,p'$ -DDT, HCB, PCBs and pentachlorobenzene (PeCB) measured at Andøya are presented in **Table 7**. Many interferences were present on the GC/ECD chromatograms from silicone strips and prevented quantification of a number of PCBs. PCB-28 was detected in silicone strips while PCB-52, PCB-153 and PCB-138 were found in SPMDs. Concentrations calculated are low and in the range 2.5-6  $\text{pg L}^{-1}$ . PeCB was measured with SPMDs and HCB was detected both with silicone strips and SPMDs. Dissolved concentrations calculated for HCB are well within a factor of two. The detection of  $\alpha$ - and  $\gamma$ -HCH was possible with silicone strips most likely due to their larger volume that resulted in lower limits of detection for compounds that equilibrate relatively rapidly. Concentrations for these HCH isomers were below 1  $\text{ng L}^{-1}$ . Only  $p,p'$ -DDE was detected in SPMDs at levels close to limits of detection.

**Table 7.** Dissolved concentrations of PCBs and organochlorines (OCs) in water measured with silicone strips and SPMDs at Andøya (concentration in  $\text{pg L}^{-1}$ ; standard deviation (SD) from replicate samplers). Concentrations above detection limit are shaded. Concentration. Especially high values are marked in red.

	Silicone strips		SPMDs	
	Cw ( $\text{pg L}^{-1}$ )	SD	Cw ( $\text{pg L}^{-1}$ )	SD
PCB-28	4.6	0.1	<2	
PCB-52	<i>i</i>		3.5	1.1
PCB-101	<i>i</i>		<30	
PCB-118	<4		<3	
PCB-105	<i>i</i>		<3	
PCB-153	<i>i</i>		6.0	0.5
PCB-138	<4		2.5	0.1
PCB-156	<i>i</i>		<4	
PCB-180	<4		<4	
PCB-209	<5		<6	
PeCB	<16.7		15	3
$\alpha$ -HCH	467	32	<60	
HCB	45	4	29	2
$\gamma$ -HCH	366*		<200	
$p,p'$ -DDE	<5.2		4.2	0.3
$p,p'$ -DDT	<6.8		<3.5	

*i*: Interferences on the GC/ECD chromatogram

\*: compound detected in one of two replicates only

**Table 8** and **Table 9** show dissolved concentrations of PCBs and other organochlorines measured with silicone strips and SPMDs at Bjørnøya for Periods 1 and 2, respectively. PCB concentrations are all below limits of detection, despite these being in the range 3-10 pg L<sup>-1</sup> for most congeners. The longer exposure time of Period 2 resulted in the detection of more compounds (e.g.  $\gamma$ -HCH in one sampler). Some differences in concentrations obtained with silicone strips or SPMDs can be observed, however differences in concentrations do not amount to more than a factor of 5 (e.g. PeCB). Because of the specific characteristics of the samplers (e.g type of polymer or polymer thickness), it may be that masses of contaminants at equilibrium accumulated by both types of samplers are representative of different lengths of exposure. Considering all possible sources of uncertainty on these measurements, this is respectable. Within sampler-type comparisons show that data from the two exposure periods are consistent.

**Table 8.** Dissolved concentrations of PCBs and organochlorines (OCs) in water measured with silicone strips and SPMDs at Bjørnøya during Period 1 (concentration in pg L<sup>-1</sup>; standard deviation (SD) from replicate samplers). Concentrations above detection limit are shaded. Especially high values are marked in red.

	Silicone strips		SPMDs	
	Cw (pg L <sup>-1</sup> )	SD	Cw (pg L <sup>-1</sup> )	SD
PCB-28	<6		<3	
PCB-52	<7		<3	
PCB-101	i		<28	
PCB-118	<7		<3	
PCB-105	i		<3	
PCB-153	i		<5	
PCB-138	<8		<4	
PCB-156	<8		<5	
PCB-180	<8		<6	
PCB-209	<9		<9	
PeCB	28.7	0.7	5.3	0.1
$\alpha$ -HCH	1054	88	<60	
HCB	117	9	48.2	2.5
$\gamma$ -HCH	454*		<210	
<i>p,p'</i> -DDE	<6		2.3	
<i>p,p'</i> -DDT	<12		<5	

i: Interferences on the GC/ECD chromatogram  
 \*: compound detected in one of two replicates only

**Table 9.** Dissolved concentrations of PCBs and organochlorines (OCs) in water measured with silicone strips and SPMDs at Bjørnøya during Period 2 (concentration in  $\text{pg L}^{-1}$ ; standard deviation (SD) from replicate samplers). Concentrations above detection limit are shaded. Especially high values are marked in red.

	Silicone strips		SPMDs	
	Cw ( $\text{pg L}^{-1}$ )	SD	Cw ( $\text{pg L}^{-1}$ )	SD
PCB-28	<4		<2	
PCB-52	<4		<2	
PCB-101	i		<24	
PCB-118	<5		<3	
PCB-105	i		<3	
PCB-153	i		<4	
PCB-138	<5		<3	
PCB-156	<5		<4	
PCB-180	<5		<5	
PCB-209	<6		<7	
PeCB	16.4	1.5	6.0	2.5
$\alpha$ -HCH	828	14	71	
HCB	78	3	48	12
$\gamma$ -HCH	393*		<210	
<i>p,p'</i> -DDE	<4		2.3	0.5
<i>p,p'</i> -DDT	<8		<3.8	

i: Interferences on the GC/ECD chromatogram  
 \*: compound detected in one of two replicates only

Isomers of HCH were detected in some but not all samplers from all three stations (**Table 7**, **Table 8** and **Table 9**). The table below (**Table 10**) presents the concentrations measured in the present study and compares these values to data found in the literature. Passive sampling data are scarce or non-existent, and most data is based on high volume water sampling. Based on our limited dataset,  $\alpha/\gamma$ -HCH ratio appears close or below 1 at Andøya and generally shows slightly higher concentrations for Bjørnøya. There is some uncertainty regarding the sampler-water interaction ( $\log K_{sw}$ ) values for silicone strips used here and data should be treated with care. Values of  $K_{sw}$  were obtained from other researchers (F. Smedes; personal comm.). This data in **Table 10** is however in agreement with data from Lakaschus *et al.* (2002). In addition, the difference in isomer concentrations observed at Bjørnøya supports the current notion that there is distillation of the  $\gamma$ -isomer during air transport above the Atlantic Ocean (the ocean acts as a sink). This process increases the relative level of the  $\alpha$ -isomer in the air in the Arctic and results in increases in concentrations of  $\alpha$ -HCH in Arctic water. It has been postulated that such a phenomenon may not be seen for sampling near coastal areas of Norway as these may be impacted by sources on land. Photo-isomerisation processes resulting in the conversion of the  $\gamma$ -HCH into  $\alpha$ -HCH may also be responsible for the relative concentrations of the two isomers.

**Table 10.** Water concentrations of  $\alpha$ - and  $\gamma$ -HCH observed in this study (silicone strip data) and found in the literature and resulting isomer ratios.

Site/Coordinates	Concentration ( $\text{pg L}^{-1}$ )			
	$\alpha$ -HCH	$\gamma$ -HCH	$\alpha/\gamma$ -HCH ratio	
Andøya	467	366	1.3	This study
Bjørnøya	1054/828	454/393	2.3/2.1	This study
N75 E14	59	72	0.8	Lakaschus <i>et al.</i> (2002)
N59.8 E42	194	504	0.4	Lakaschus <i>et al.</i> (2002)
Near Greenland	0.9	0.2	4.5	Summarised in Walker <i>et al.</i> (1999)
E. Arctic Ocean	0.91	0.27	1.5-5	

Very few passive sampling measurements of *p,p'*-DDE and HCB for Arctic waters exist. Booij *et al.* (2007) measured HCB with SPMDs during a cruise in the English Channel/Atlantic. Concentrations measured on the Norwegian coast are in agreement with the levels they observed (**Table 11**). Concentrations observed at Bjørnøya are just under an order of magnitude higher than their data. Data summarised by Barber *et al.* (2005) indicated seawater concentrations for HCB generally in the range



5-27 pg L<sup>-1</sup>. DDT's degradation product *p,p'*-DDE was also measured as part of the study of Booij *et al.* (2007) and was found at concentrations in the low pg L<sup>-1</sup> level, close to those measured at Andøya and Bjørnøya.

**Table 11.** Water concentrations of *p,p'*-DDE and HCB observed in this study (silicone strip/SPMD) and found in the literature.

Site/Coordinates	Concentration (pg L <sup>-1</sup> )		
	<i>p,p'</i> -DDE	HCB	
Andøya	4.2	29/45	This study
Bjørnøya	2.3	48-117	This study
English Channel/Atlantic ocean	1.4	9	Booij <i>et al.</i> (2007)
Seawater (active sampling)		5-27	Barber <i>et al.</i> (2005)

### 3.1.4 Polybrominated diphenylethers (PBDEs)

Dissolved concentrations of PBDEs measured with silicone strips and SPMDs at Andøya and Bjørnøya (Periods 1 and 2) are given in *Table 12*, *Table 13* and *Table 14*. Two PBDEs, the tetrabromodiphenylether PBDE-47 and the pentabromodiphenylether PBDE-99, are consistently detected in silicone strips and SPMDs at all sites. For Andøya, PBDE-28 was also found above limits of detection in SPMDs. Concentrations of PBDE-47 and PBDE-99 measured with silicone strips and SPMDs were very consistent (*Table 12*) while differences between data from the two types of samplers were more significant for the data from Bjørnøya (*Table 13* and *Table 14*). The cold temperatures of the water at Bjørnøya may have affected the sampling with the two types of samplers differently. Concentrations are in the low  $\text{pg L}^{-1}$  level. The reproducibility of the measurement of PBDE-47 with silicone is generally poorer than with SPMDs as the data from replicate samplers show significant variability indicated by the higher standard deviations for the silicone results. PBDE-100 was detected during the longest exposure of SPMDs and an estimate of concentration is  $0.40 \text{ pg L}^{-1}$ . PBDE-209 was consistently measured in extract from silicone strips deployed in water but was also found in one trip control sampler above limits of detection. Dissolved concentrations were calculated but significant uncertainty is associated with  $\log K_{\text{sw}}/\log K_{\text{ow}}$  values. PBDE-209 was detected in SPMD extracts from Bjørnøya (Period 1) but while trip controls were below limits of detection, levels in some preparation control samplers were above limits of detection. Contamination of SPMDs with PBDE-209 during preparation is possible and may be relatively variable.

**Table 12.** Dissolved concentrations of PBDEs in water measured with silicone strips and SPMDs at Andøya (concentration in  $\text{pg L}^{-1}$ ; standard deviation (SD) from replicate samplers). Concentrations above detection limit are shaded.

	Silicone strips		SPMDs	
	Cw ( $\text{pg L}^{-1}$ )	SD	Cw ( $\text{pg L}^{-1}$ )	SD
<b>PBDE-28</b>	<0.9		2.1	1.8
<b>PBDE-47</b>	4.8	1.4	1.9	0.3
<b>PBDE-49</b>	<0.9		<0.7	
<b>PBDE-66</b>	<0.9		<0.6	
<b>PBDE-71</b>	<0.9		<0.7	
<b>PBDE-77</b>	<0.9		<0.9	
<b>PBDE-85</b>	<1.0		<0.8	
<b>PBDE-99</b>	0.8	0.2	0.77	0.07
<b>PBDE-100</b>	<0.2		<1.8	
<b>PBDE-138</b>	<1.1		<1.4	
<b>PBDE-153</b>	<1.1		<1.4	
<b>PBDE-154</b>	<1.1		<1.4	
<b>PBDE-183</b>	<1.2		<3	
<b>PBDE-196</b>	<1.3		<11	
<b>PBDE-205</b>	<1.4		<20	
<b>PBDE-209</b>	4.4*	1.0	<50	

\*One trip control sampler contained approximately 0.85 ng BDE209 (LOD = 0.5 ng BDE209 per sampler), BDE209 was consistently detected in water-deployed silicone strips, but levels were below LODs in all other trip controls.

**Table 13.** Dissolved concentrations of PBDEs in water measured with silicone strips and SPMDs at Bjørnøya during Period 1 (concentration in  $\mu\text{g L}^{-1}$ ; standard deviation (SD) from replicate samplers). Concentrations above detection limit are shaded.

	Silicone strips		SPMDs	
	Cw ( $\mu\text{g L}^{-1}$ )	SD	Cw ( $\mu\text{g L}^{-1}$ )	SD
PBDE-28	<1.7		<0.1	
PBDE-47	6.0	6.1	0.46	0.05
PBDE-49	<1.7		<0.1	
PBDE-66	<1.7		<0.1	
PBDE-71	<1.7		<0.1	
PBDE-77	<1.7		<0.5	
PBDE-85	<1.8		<0.1	
PBDE-99	7.5	0.1	0.33	0.07
PBDE-100	<1.1		<0.2	
PBDE-138	<2.0		<0.1	
PBDE-153	<2.0		<0.1	
PBDE-154	<2.0		<0.1	
PBDE-183	<2.2		<0.1	
PBDE-196	<2.4		<0.3	
PBDE-205	<2.7		<0.3	
PBDE-209	4.8*	0.2	1.3**	0.2

\*One trip control sampler contained approximately 0.85 ng BDE209 (LOD = 0.5 ng BDE209 per sampler), BDE209 was consistently detected in water-deployed silicone strips, but levels were below LODs in all other trip/preparation controls.

\*\*Trip controls were below LOD but preparation controls were above LODs

**Table 14.** Dissolved concentrations of PBDEs in water measured with silicone strips and SPMDs at Bjørnøya during Period 2 (concentration in  $\mu\text{g L}^{-1}$ ; standard deviation (SD) from replicate samplers). Concentrations above detection limit are shaded.

	Silicone strips		SPMDs	
	Cw ( $\mu\text{g L}^{-1}$ )	SD	Cw ( $\mu\text{g L}^{-1}$ )	SD
PBDE-28	<1.0		<0.1	
PBDE-47	7.0	4.3	0.29	0.03
PBDE-49	<1.0		<0.1	
PBDE-66	<1.0		<0.1	
PBDE-71	<1.0		<0.1	
PBDE-77	<1.0		<0.5	
PBDE-85	<1.1		<0.1	
PBDE-99	5.5	0.4	0.19	0.03
PBDE-100	<0.7		0.40	0.05
PBDE-138	<1.2		<0.1	
PBDE-153	<1.2		<0.1	
PBDE-154	<1.2		<0.1	
PBDE-183	<1.3		<0.15	
PBDE-196	<1.5		<0.3	
PBDE-205	<1.6		<0.3	
PBDE-209	2.1*		<0.5	

\*One trip control sampler contained approximately 0.85 ng BDE209 (LOD = 0.5 ng BDE209 per sampler), BDE209 was consistently detected in water-deployed silicone strips, but levels were below LODs in all other trip controls.

### 3.1.5 Comparison of the two exposure periods for Bjørnøya

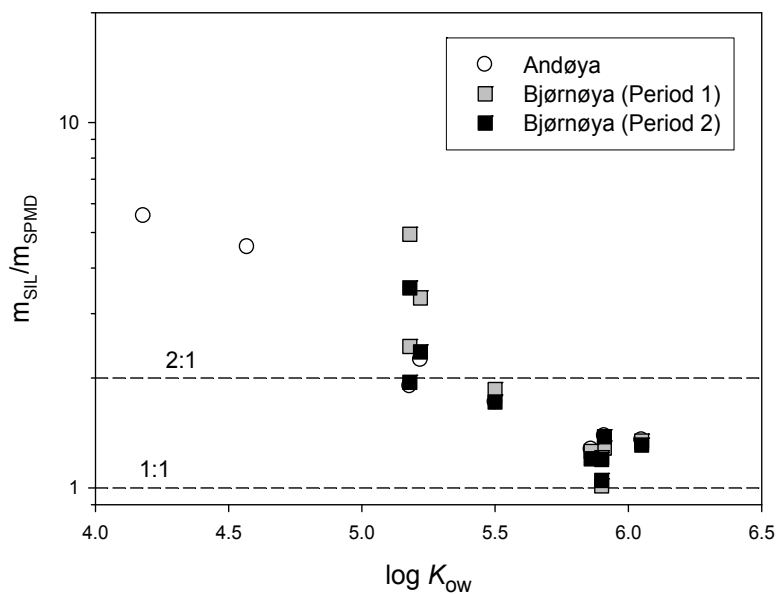
Silicone strips and SPMDs were deployed at Bjørnøya for two overlapping periods. Samplers from Period 1 were exposed for 263 days (05.12.2009-25.08.2010) while those from Period 2 exposed for 362 days (28.08.2009-25.08.2010). PRC dissipation (data not shown) was in agreement with relative exposure times. **Table 15** presents ratios of concentrations obtained from the two exposure periods for each type of samplers. If dissolved contaminant concentrations remained constant through the year, ratios close to 1 should be observed. Ratios generally vary between 0.6 and 1.2 for both samplers. These differences can be due to differences in concentrations for the two exposures, effect of increasing levels of biofouling for longer exposures, impact of the mode of estimation of concentrations (and PRC data). Considering the year-long exposure of the samplers at these sites, these differences are relatively minor.

**Table 15.** Ratios of water concentrations measured at Bjørnøya during Period 2 (362 days) over those measured during Period 1 (263 days) with silicone strips and SPMDs

	Silicone strips	SPMD
	$C_{w-P2}/C_{w-P1}$	$C_{w-P2}/C_{w-P1}$
PeCB	0.6	1.2
$\alpha$ -HCH	0.7	
HCB	0.7	1.0
<i>p,p'</i> -DDE		1.0
Acenaphthene	0.9	
Fluorene	0.7	
Dibenzothiophene	0.8	
Phenanthrene	0.7	
Anthracene	1.2	
Fluoranthene	0.6	1.1
Pyrene	0.7	1.1
Benz[a]anthracene	0.7	0.8
Chrysene	0.7	0.9
Benzo[b+j]fluoranthene	0.7	1.0
Benzo[k]fluoranthene	0.7	0.9
Benzo[e]pyrene	0.8	1.1
PBDE-47	1.2	0.6
PBDE-99	0.7	0.6

### 3.1.6 Comparison of data obtained with the two different types of passive samplers

Silicone strips tended to absorb higher amounts of analytes that reach equilibrium relatively fast and this allows lower limits of detection for these compounds. This can be seen on **Figure 5**, where ratios of masses absorbed by silicone strips over those absorbed by SPMDs are significantly above 1 for compounds with  $\log K_{ow} < 5.5$ . For analytes with  $\log K_{ow} > 5.5$  these ratios are closer to 1. Uptake remained linear for these compounds over the exposure times and uptake kinetics is likely to be almost entirely controlled by mass transfer in the boundary layer at the surface of the samplers.



**Figure 5.** Ratio of PAH and PCB/OC masses accumulated in silicone strips and those found in SPMDs.

### 3.1.7 Comparison of data obtained with Environmental Quality Standards (EQS) set by the European Union's Water Framework Directive

Under Water Framework Directive legislation (2000/60/EC), the European Union has established target Environmental Quality Standards (AA-EQS) for a set of priority substances (2008/105/EC) for inland and coastal waters. Assuming these concentrations (in the whole water) can also be applied for areas around Jan Mayen and Bjørnøya, they provide a basis as reference values for establishing good water quality status. Priority substances that were analysed for in passive sampler extracts from Andøya, Bjørnøya and Jan Mayen are given in **Table 16**, together with respective AA-EQS values and dissolved concentrations estimated with the passive sampling devices. One has to bear in mind that passive sampling-derived concentrations are for freely dissolved contaminants while AA-EQS values refer to "whole water" samples. On average, passive sampling-derived concentrations for Andøya and Bjørnøya are > 1000 lower than AA-EQS values for anthracene, benzo[a]pyrene and *p,p'*-DDT. Those for fluoranthene, hexachlorobenzene, pentachlorobenzene, benzo[b+k]fluoranthene are between 100 and 1000 times lower than AA-EQS values. On average, the sum of concentrations of benzo[ghi]perylene and indeno[1,2,3-cd]pyrene, and that of hexachlorocyclohexane are approximately a factor of 50 lower than EQS values. Highest PBDE concentrations were measured for PBDE-47 and PBDE-99 with concentrations between 2 and 8  $\mu\text{g L}^{-1}$  which is close to factor of 30 below EQS.

**Table 16.** EU WFD's annual average environmental quality standards (AA-EQS) for a range of priority substances that were analysed for in samplers deployed at Andøya, Bjørnøya and Jan Mayen and concentrations in water measured at these different sites.

Priority substances	AA-EQS ( $\text{ng L}^{-1}$ )	Andøya ( $\text{ng L}^{-1}$ )	Bjørnøya Period 1 ( $\text{ng L}^{-1}$ )	Bjørnøya Period 2 ( $\text{ng L}^{-1}$ )	Jan Mayen ( $\text{ng L}^{-1}$ )
Anthracene	100	0.06	0.043	0.053	-
Pentabromodiphenylether	0.2	0.0008-0.005	0.001-0.008	0.0002-0.007	-
Fluoranthene	100	1.1	0.95	0.60	-
Hexachlorobenzene	10	0.045	0.12	0.078	-
Hexachlorocyclohexane	2	0.37	0.45	0.39	-
Pentachlorobenzene	7	<0.02	0.029	0.016	-
Benzo[a]pyrene	50	0.018	<0.02	<0.009	-
Benzo[b+k]fluoranthene*	30	0.25	0.12	0.088	-
Benzo[ghi]perylene & indeno[1,2,3-cd]pyrene**	2	0.064	<0.04 <sup>a</sup>	0.025	-
Sum of DDTs***	25	-	-	-	-
<i>p,p'</i> -DDT	10	<0.007	<0.012	<0.008	-

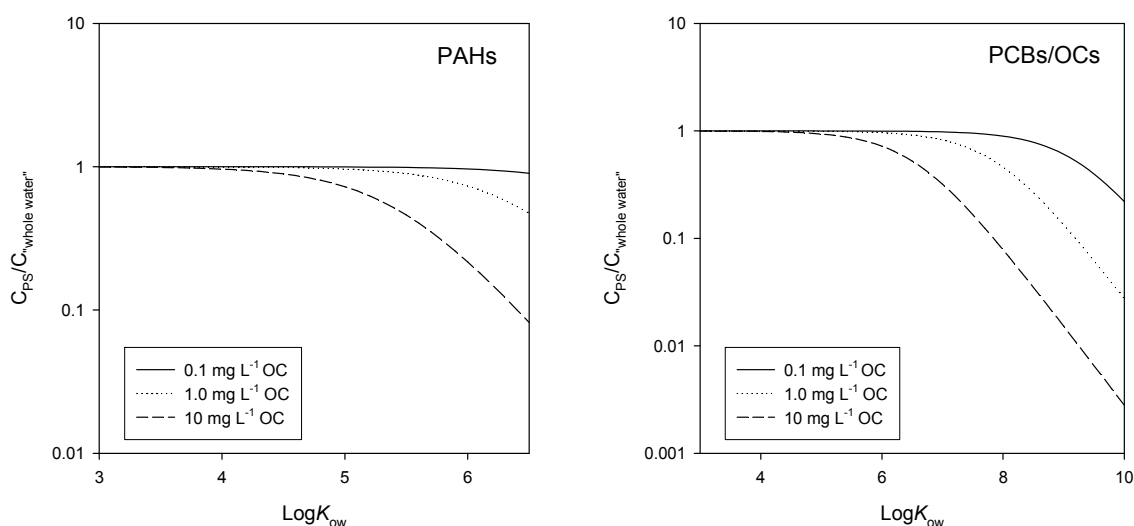
\*Sum of benzo[b]fluoranthene and benzo[k]fluoranthene

\*\*Sum of Benzo[ghi]perylene and indeno[1,2,3-cd]pyrene

\*\*\*Sum of isomers with CAS numbers: 50-29-3, 789-02-6 and 72-54-8

<sup>a</sup>Both values were below LODs

Passive sampling-derived concentrations are for freely dissolved contaminants while AA-EQS values refer to “whole water” samples. This renders their direct comparison difficult. Depending on the amount and type of organic carbon in water, a proportion (more or less significant) of contaminants will be sorbed to particulate and dissolved organic matter. Based on published organic carbon-water partition coefficients,  $K_{oc}$  (Scharwzenbach *et al.*, 2003), it is possible to estimate the fraction of the “whole water” concentration that is being measured with a passive sampler. **Figure 6** presents modelled passive sampler-derived concentrations relative to “whole water” concentrations as a function of compound’s hydrophobicity and the level of organic carbon (with no differentiation between particulate and dissolved organic carbon) in water. For example for PAHs with  $\log K_{ow}$  of 6.5 and a OC content of the water of  $1 \text{ mg L}^{-1}$ , the passive sampler-derived concentration is approximately 50 % of the “whole water” concentration. This indicates that for most substances in the table above (**Table 16**), with a total organic carbon content of the water of  $1 \text{ mg L}^{-1}$ , “whole water” concentrations are likely to be below EQS. This modelling is likely to be very uncertain for compounds such as pentabromodiphenylether with  $\log K_{ow}$  values between 6 and 10 and for which a larger proportion is likely to be associated with organic carbon in water (see **Figure 6**).



**Figure 6.** Modelled contaminant concentrations measured with passive sampling devices relative to “whole water” concentrations accounting for contaminant partitioning to organic carbon (OC) at three levels ( $0.1$ ,  $1.0$  and  $10 \text{ mg L}^{-1}$ ).

### 3.1.8 Comparison of data obtained with concentrations in biota and in sediments

As part of the overall project (Green *et al.*; 2010) contaminant concentrations were also measured in bed sediments (top 2 cm layer) and in cod liver (*Gadus morhua*) at sampling sites at Andøya and Bjørnøya. It was therefore possible to calculate apparent distribution coefficients from concentrations of contaminants accumulated in the bottom sediments ( $C_{sed}$ ), the fraction of organic carbon of the sediment ( $f_{oc}$ ) and those for contaminants dissolved in the water column ( $C_w$ ).

$$K_{oc} = \frac{C_{sed} / f_{oc}}{C_w}$$

These distribution coefficients ( $\log K_{oc}$ ) are presented in **Table 17** for PAHs and **Table 18** for PCBs/OCs and PBDEs.

**Table 17.** Apparent distribution coefficient (normalised to organic carbon content of the sediment),  $\log K_{oc}$  ( $L\ kg^{-1}\ OC$ ) for PAHs in the top layer of bed sediment and dissolved in the water column.  $\log K_{ow}$  values are given for information.

	$\log K_{ow}$	$\log K_{oc}$ ( $L\ kg^{-1}\ OC$ )*	
		Andøya	Bjørnøya
<b>Fluorene</b>	4.18	6.44	6.49
<b>Dibenzothiophene</b>	4.38		6.93
<b>Phenanthrene</b>	4.57	6.55	6.76
<b>Anthracene</b>	4.54		6.52
<b>Fluoranthene</b>	5.22	6.41	6.55
<b>Pyrene</b>	5.18	6.82	6.94
<b>Benzo[a]anthracene</b>	5.91	7.54	7.90
<b>Chrysene</b>	5.86	7.69	8.22
<b>Benzo[b+j]fluoranthene</b>	5.90	7.52	7.94
<b>Benzo[k]fluoranthene</b>	5.90	7.74	7.56
<b>Benzo[a]pyrene</b>	6.05	7.97	
<b>Perylene</b>	6.25	7.88	
<b>Indeno[1,2,3-cd]pyrene</b>	6.50	8.25	8.25
<b>Benzo[ghi]perylene</b>	6.50	8.51	8.57

\*Data given only when both sediment and water concentrations were > LODs

For PAHs,  $\log K_{oc}$  values are in the range 6.44-8.57 and appear to increase with compounds hydrophobicity. Only minor differences in values for the two sites can be observed. These values tend to be higher (by 1.5-2.0 log units) than those expected based on empirical relationships (Scharwzenbach *et al.*, 2003 and Karrickhoff *et al.*, 1979) which could indicate that these are not in equilibrium or that concentrations in the water column are not directly related to those in the bottom sediment. For PCBs/OCs and PBDEs,  $\log K_{oc}$  values range from 3.33 for  $\alpha$ -HCH to 7.11 for PBDE-209. The  $\log K_{oc}$  value for  $\gamma$ -HCH appears to be slightly higher than for the  $\alpha$ -isomer and this is in agreement with their respective  $\log K_{ow}$  values.



**Table 18.** Apparent distribution coefficient (normalised to organic carbon content of the sediment),  $\log K_{oc}$  ( $L\ kg^{-1}\ OC$ ) for PCBs, OCs and PBDEs in the top layer of bed sediment and dissolved in the water column.  $\log K_{ow}$  values are given for information.

	$\log K_{ow}$	$\log K_{oc}$ ( $L\ kg^{-1}\ OC$ )*	
		Andøya	Bjørnøya
PCB-28	5.67	5.95	
PCB-52	5.84	5.84	
$\alpha$ -HCH	3.81	3.33	3.52
HCB	5.50	4.76	5.52
$\gamma$ -HCH	4.14		4.02
<i>p,p'</i> -DDE	6.29	6.22	
PBDE-47	6.60	6.31	7.00
PBDE-99	7.22	6.82	5.98
PBDE-209	10.30		7.11

\*Data given only when both sediment and water concentrations were > LODs

Bioaccumulation factors (BAFs) for compounds (some PCBs, OCs and PBDEs) measured in cod liver from Andøya and Bjørnøya are presented in **Table 19**. Values obtained tend to be in good agreement with  $\log K_{ow}$  of the respective compounds.

**Table 19.** Bioaccumulation factor (normalised to lipid content of the liver),  $\log BAF$  ( $L\ kg^{-1}\ lipid$ ) for PCBs/OCs and PBDEs in the top layer of bed sediment and dissolved in the water column.  $\log K_{ow}$  values are given for information.

	$\log K_{ow}$	$\log BAF$ ( $L\ kg^{-1}\ lipid$ )*	
		Andøya	Bjørnøya
PCB-28	5.67	5.78	
PCB-52	5.84	6.25	
PeCB	5.18	5.21	
$\alpha$ -HCH	3.81	3.60	3.59
HCB	5.50	5.48	5.65
$\gamma$ -HCH	4.14		3.85
<i>p,p'</i> -DDE	6.29	7.07	
PBDE-28	5.98	5.16	
PBDE-47	6.60	6.19	6.07

\*Data given only when both cod liver and water concentrations were > LODs

## 3.2 Contaminant concentrations in air

The individual periods have been averaged over the whole sampling period to make it more comparable with the measurements in the ocean. Further, only a selection of the compounds measured are reported in this chapter to compare with other studies not with those measured in water. However all the individual data points are found in Appendix A1. The average was weighted with number of days for each sampling period and data below detection limit was given half the detection limit. Data for PBDE is as mentioned in the introduction not included due to high uncertainty in the data and the fact that most of most compounds are under the detection limit ( $0.01 \text{ pg m}^{-3}$ ).

### 3.2.1 Polycyclic aromatic hydrocarbons (PAHs)

The average concentration of the 8 different PAHs as shown in *Table 20* was quite similar ( $1\text{-}2 \text{ ng m}^{-3}$ ) for all the sites with a small decrease from distance to the mainland and to the main emissions sources, though the difference is too small to be called significant. The level is comparable to what was reported in the passive sampler study conducted in 2006 (Halse *et al.*, 2011). The more abundant PAHs include phenanthrene and fluorene, and the contribution from heavier PAHs with higher affinity for particulate matter is much lower.

*Table 20. Concentrations of selected PAH ( $\text{ng m}^{-3}$ ) in air measured with passive samplers.*

	Andøya	Bjørnøya	Jan Mayen
<b>Deployment</b>	<b>29.11.09</b>	<b>29.12.09</b>	<b>05.01.10</b>
<b>Retrieval</b>	<b>16.08.10</b>	<b>28.08.10</b>	<b>29.07.10</b>
<b>Fluorene</b>	0.7	0.6	0.7
<b>Phenanthrene</b>	0.7	0.5	0.3
<b>Anthracene</b>	0.01	0.005	0.002
<b>Fluoranthene</b>	0.2	0.2	0.1
<b>Benz[a]anthracene</b>	0.01	0.003	0.001
<b>Chrysene</b>	0.02	0.016	0.012
<b>Benzo[a]pyrene</b>	0.01	0.001	0.003
<b>Pyrene</b>	0.08	0.06	0.03
<b>Sum 8 PAH</b>	<b>1.7</b>	<b>1.3</b>	<b>1.1</b>

### 3.2.2 Polychlorinated biphenyls (PCBs) and other organochlorines (OCs)

The concentration of PCBs are shown in *Table 21*, and the level is somewhat higher at Andøya compared with the two other sites, and the difference is relatively larger for the heavier PCBs. This is a general pattern due to the more limited long-range atmospheric transport potential of heavier PCBs with distance from sources (Wania and Daly, 2002).

The concentration of HCB on the other hand is highest at Jan Mayen and lowest at Andøya, similar is seen for pentachlorobenzene (PeCB). These are also among the most volatile substances investigated and which may have reached equilibrium during the sampling periods. Colder air temperatures which are typically also correlated with wind speeds and expected at the northernmost sites will favour enhanced partitioning and uptake from the gas phase to the PUF, leading to enhanced relative amounts sequestered by the northernmost samplers, and could thus help explain the elevated air concentrations at the northernmost sites. This also incidentally illustrates some of the limitations of the PAS method when used at cold and windy sites in the Arctic. The levels of HCB is also significantly higher than

seen in the average concentration of HCB in the passive campaign in Europe in 2006 ( $49 \pm 18 \text{ pg m}^{-3}$ ) For active samples the HCB concentrations are quite similar comparing the sites in southern Norway (Birkenes) and Zeppelin (Svalbard) with levels between  $65\text{-}85 \text{ pg m}^{-3}$  the last years (Aas *et al.*, 2010).

For chlordanes the level between sites are very comparable; furthermore, the levels of the individual chlordanes as well as the sum of the selected four compounds, are very similar to the average European level in air experienced in the passive campaign in summer 2006, i.e.  $3.5 \pm 2.7 \text{ pg/m}^3$  (Halse *et al.*, 2011).

The  $\alpha$ -HCH concentration is higher at the two most Arctic sites compared two Andøya. This may reflect that the ocean can act as a source of  $\alpha$ -HCH and/or enhanced uptake because of cold temperatures and enhanced wind speeds, though the uncertainty in the method is too high to conclude on this. For the regular monitoring with active sampler the levels of  $\alpha$ -HCH at Birkenes and Zeppelin is both around  $7\text{-}9 \text{ pg/m}^3$ , (Aas *et al.*, 2010). As expected because of a more limited long range transport potential due to enhanced potential for wash-out by rain, the level of  $\gamma$ -HCH is lower than  $\alpha$ -HCH in these arctic sites and comparable to each other.

For DDT the highest level is seen at Bjørnøya, and for all sites the  $p,p'$ -DDE is the most important isomer. The level is however higher than what is seen in the active sampler at Zeppelin,  $0.43 \text{ pg m}^{-3}$  in 2009 (Aas *et al.*, 2010).

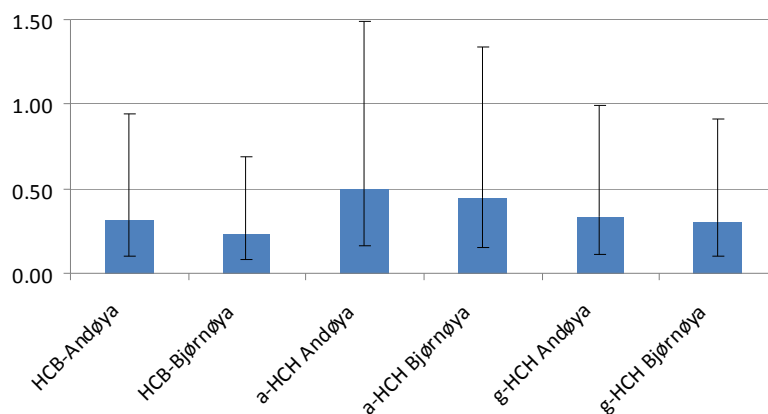
**Table 21.** Concentrations of selected PCBs and OCs ( $\mu\text{g m}^{-3}$ ) in air measured with passive samplers.

Deployment Retrieval	Andøya	Bjørnøya	Jan Mayen
	29.11.2009 16.08.2010	29.12.2009 28.08.2010	05.01.2010 29.07.2010
<b>PCB-28</b>	3.5	2.1	1.7
<b>PCB-52</b>	2.5	2.3	2.0
<b>PCB-101</b>	2.5	1.4	1.1
<b>PCB-118</b>	0.6	0.5	0.3
<b>PCB-138</b>	1.7	0.5	0.4
<b>PCB-153</b>	2.3	0.8	0.6
<b>PCB-180</b>	0.8	0.2	0.1
<b>Sum 7 PCB</b>	<b>14</b>	<b>8</b>	<b>6</b>
<b>HCB</b>	66	107	129
<b>PeCB</b>	9	12	16
<b>trans-Chlordane</b>	0.6	1.0	1.0
<b>cis-Chlordane</b>	1.4	2.4	2.2
<b>trans-Nonachlor</b>	1.2	2.0	19
<b>cis-Nonachlor</b>	0.1	0.1	0.1
<b>Sum 4 chlordanes</b>	<b>3.3</b>	<b>5.6</b>	<b>5.2</b>
$\alpha$ -HCH	12	21	19
$\gamma$ -HCH	2.9	3.1	2.6
p,p'-DDE	1.8	4.3	2.2
p,p'-DDD	0.06	0.07	0.2
o,p'-DDT	0.5	0.9	07
p,p'-DDT	0.3	0.6	0.3
<b>Sum 4 DDTs</b>	<b>2.7</b>	<b>5.8</b>	<b>3.4</b>

### 3.3 Comparison of air and water concentrations for selected compounds

Transfer of POPs from air to seawater through diffusion represents a key pathway for which these contaminants enter the marine environment (Wania *et al.*, 1998). Diffusive exchange also occurs in the opposite direction from seawater to air, and the net direction and magnitude of this exchange process depends on concentration gradients between these two media, temperatures in air and seawater, wind speed and the physical-chemical properties of the compound of interest. There are some fundamental challenges involved in any estimate of diffusive air-water exchange and in particular under circumstances when air and seawater are close to equilibrium and/or when the compounds of interest are close to detection limits (Bruhn *et al.*, 2003). Nevertheless, as passive samplers in air and seawater have been co-located at both Bjørnøya and Andøya, it is possible to take this opportunity to assess the direction of fluxes for selected compounds. This may help guide further research needs.

In **Figure 7**, we have plotted the fugacity ratios for selected POPs (HCB,  $\alpha$ -HCH and  $\gamma$ -HCH) using the passive air data given in **Table 21** and passive water data from **Table 7**, **Table 8** and **Table 9**. For these calculations, information on physical-chemical properties and the temperature dependence of these properties were taken from Shen and Wania (2005) for HCB and Xiao *et al.* (2004) in the case of HCH isomers.  $F_{\text{air}}/F_{\text{water}}$  fugacity ratios are generally below 1, indicating an air-to-water flux. However, based on the uncertainty associated with both air and water concentration estimates, the range of these values is wide (error bars on **Figure 7** reflect the uncertainty associated with air data only). An additional bias of a factor of two can be expected for passive sampling data in water.



**Figure 7.** Estimates of fugacity ratios ( $f_{\text{air}}/f_{\text{water}}$ ) for selected compounds at two sampling sites. A ratio above 1 indicates an air-to-water flux while a ratio below 1 is indicative of a water-to-air flux. Error bars indicate minimum and maximum fugacity ratios based on an uncertainty in air concentrations of a factor of 3. Additional uncertainty and bias in water concentrations are not shown.

## 4. Conclusions

### 4.1 Passive sampling in water

Passive sampling devices (semipermeable membrane devices and silicone strips) were deployed at three sites, namely Andøya, Bjørnøya and Jan Mayen. Useful and novel data was obtained from the first two sites while samplers exposed at the latter were lost due to the sea conditions. SPMDs and silicone strips were also exposed in the air at those three sites (data analysis and interpretation is forthcoming). The relatively lengthy deployments for samplers exposed at Andøya and Bjørnøya ensured improved limits of detection. The longer deployment at Bjørnøya enabled the quantification of a large number of compounds (e.g. for PAHs). For certain compounds, it was possible to compare dissolved water concentrations with those measured in the whole sediment and accumulated in fish (cod) liver.

#### Detailed conclusions of this work are:

- The quality of trip control samplers was adequate, though procedures aiming to minimise possibilities for contamination of samplers during exposure and retrieval manipulations should be optimised.
- Dissipation of performance reference compounds allowed the quantification of contaminant exchange kinetics between water and the samplers. In turn, sampling rates could be calculated for the period of deployment.
- PAH limits of detection from 12 month exposures are adequate, unless we attempt to increase the size of the samplers.
- PCB concentrations in water are very low and close to or below limits of detection for both Andøya and Bjørnøya. These limits of detection are in the low  $\text{pg L}^{-1}$ .
- Limits of detection for PeCB and HCB are adequate.
- Limits of detection for *p,p'*-DDE and HCH isomers are in a similar range as that of concentrations measured. Silicone strips appear to absorb higher amount of HCH isomers than SPMDs. This could be further improved by optimising sampler properties.
- PBDE-47 and PBDE-99 are consistently found above limits of detection.
- The performance of silicone strips and SPMDs is similar. It is possible however that discrepancies in the data obtained with the two types of samplers is the result their efficiency at low temperature.
- Unless sampler conformation is radically changed, exposure time should be kept to 12 months for deployments in water. Alternatively sampler exposures could be undertaken using alternative cages to enable higher water turbulences near the sampler surface and hence higher sampling rates (and lower limits of detection).
- The exposure of time-integrative absorption-based samplers (such as SPMDs and silicone strips) in the air resulted in the detection of some contaminants (forthcoming results).
- In most cases, estimates of contaminant concentrations in water appear to be well below environmental quality standards set by the European Union's Water Framework Directive (WFD)
- Passive samplers are able to provide information on contaminant levels in locations where it is generally difficult to obtain samples of biota. In addition, they appear very suited to the evaluation of long term trends in concentrations.
- Rough estimates of air-water exchange were calculated from air and water concentrations; however these need to be used carefully since both air and water data are subject to significant uncertainty and bias.

**Identified future research work:**

- It would be useful to estimate the effect temperature and salinity on sampler-water partition coefficients (for SPMDs and silicone strips) in order to improve estimates of dissolved contaminant concentrations in water. With respect of the sampling rates, it would also be useful to assess whether sampling rates are constant throughout the 12 month exposure or whether substantial differences exist (with seasons, temperature or biofouling).
- The exposure of time-integrative absorption-based samplers (such as SPMDs and silicone strips) both in water and in the air should be pursued. This will enable us to compare directly freely available contaminant concentrations in air and water and allow us to estimate air-water concentration gradient and fluxes. This work was initiated in 2009 and ought to be pursued.
- It may be useful to extend this study to other contaminants or emerging substances of interest. Some of the proposed additional priority substances (as part of the European Union's WFD or MFSD) could in the future be screened for as part of these studies. These include hexabromocyclohexane (HBCD), dioxins, pesticides such as cypermethrin, dichlorvos or cybutryne, or pharmaceuticals and personal care products such as diclofenac or ibuprofen.
- Other types of passive sampling devices could be used to extend the range of substances that can be screened for during such monitoring. This range could be based on many emerging substances, including many more polar compounds.
- This work could benefit from using an alternative sampling procedure (to be discussed).

## 4.2 Air monitoring

The results obtained on the basis of passive air samplers are broadly consistent with results from past findings and active air samplers, yet also revealed difficulties when applying this method at Arctic sites, which are mainly attributed to the climatic conditions experienced (colder temperatures and elevated wind speeds). Thus, the results presented are only expected to represent the “true” air concentrations within a factor of ~2-3. This needs to be taken into consideration when interpreting the results and if these data are to be used to discuss potential equilibrium status and net flux directions between air and surface seawater.

### **Main conclusions:**

- Levels of POPs in air have successfully been measured at three sites (Jan Mayen, Bjørnøya and Andøya) using passive air samplers (PUFs).
- Air concentrations have been back-calculated using depuration compounds, providing estimates of in situ uptake rates.
- The windy conditions often experienced at these Arctic sites lead to uncertainties in back-calculated air concentrations.
- The uncertainty in the PAS method (i.e. a factor 2-3) combined with the limited number of stations (3) makes it difficult to infer something about spatial patterns in air on the basis of the existing dataset.

### **Research needs/further work may include:**

- Adding a number of additional PAS sites along the Norwegian coast to include spatial coverage.
- Shorter sampling periods (e.g. 4-6 weeks) to obtain more information on seasonal variability.
- Co-deployment of passive air samplers at the Norwegian permanent sampling stations sites (Birkenes, Andøya, Zeppelin) to further evaluate and discuss the complementary features of the two sampling approaches (active versus passive).
- Screening for organic contaminants of emerging concern, such as various perfluorinated compounds and siloxanes, using PAS.
- Test of alternative PAS sampling approaches which may be more suitable for the climatic conditions experienced (e.g. XAD-resins in hollow metal tubes).
- A more in-depth evaluation of the feasibility of using passive sampling strategies in air and water to assess net flux direction, preferably combined with active sampling strategies in both media to evaluate the merit of passive versus active sampling strategies in this context, and with chemical analysis preferably carried out at a single laboratory to avoid interlaboratory differences.



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## **Appendix A. Concentration of POPs in air from passive samplers**



Table A.1 Concentration of the all PCB in air in the individual samples at Andøya, Bjørnøya and Jan Mayen and the averages for the periods,  $\text{pg m}^{-3}$ .

	IUAPC no	Andøya			Bjørnøya				Jan Mayen			
		period 1	period 2	average	period 1	period 2	period 3	average	period 1	period 2	period 3	average
start time		29.11.2009	26.02.2010	29.11.2009	28.08.2009	29.12.2009	14.04.2010	29.12.2009	05.10.2009	05.01.2010	08.04.2010	05.01.2010
end time		26.02.2010	16.08.2010	16.08.2010	29.12.2009	13.04.2010	28.08.2010	28.08.2010	05.01.2010	08.04.2010	29.07.2010	29.07.2010
nr of days		89	171	260	123	105	136	364	92	93	112	297
		pg/m3	pg/m3	pg/m3	pg/m3	pg/m3	pg/m3	pg/m3	pg/m3	pg/m3	pg/m3	pg/m3
PeCB		19	4	9	15	14	7	12	20	18	10	16
HCB		93	51	66	105	138	86	107	135	158	102	129
2,2',5'-TriCB	18	4.2	3.0	3.4	4.5	5.4	0.9	3.4	3.6	4.7	1.4	3.1
2,4,4'-TriCB	28	3.3	3.7	3.5	2.6	3.3	0.6	2.1	2.0	2.7	0.7	1.7
2,4',5'-TriCB	31	3.0	3.2	3.1	2.5	3.1	0.6	2.0	1.9	2.6	0.7	1.7
2',3,4'-TriCB	33	1.8	2.0	2.0	1.5	1.9	0.3	1.2	1.0	1.6	0.4	1.0
3,4,4'-TriCB	37	0.5	1.0	0.8	0.2	0.3	0.1	0.2	0.1	0.2	0.04	0.1
2,2',4,4'-TetCB	47	1.0	0.9	0.9	0.9	1.2	0.3	0.7	0.6	1.0	0.3	0.6
2,2',5,5'-TetCB	52	2.6	2.4	2.5	2.8	3.5	0.9	2.3	2.2	3.1	1.1	2.0
2,3',4,4'-TetCB	66	0.9	1.4	1.2	0.7	0.8	0.2	0.5	0.4	0.6	0.2	0.4
2,4,4',5'-TetCB	74	0.6	0.7	0.7	0.4	0.6	0.1	0.4	0.3	0.4	0.1	0.3
2,2',4,4',5'-PenCB	99	0.5	0.5	0.5	0.7	1.0	0.3	0.6	0.5	0.7	0.2	0.5
2,2',4,5,5'-PenCB	101	1.6	2.9	2.5	1.7	2.2	0.7	1.4	1.2	1.7	0.5	1.1
2,3,3',4,4'-PenCB	105	0.2	0.2	0.2	0.2	0.3	0.1	0.2	0.1	0.2	0.05	0.1
2,3,4,4',5'-PenCB	114	<0.02	0.1	0.05	0.01	0.02	<0.01	0.01	<0.01	<0.01	<0.01	0.01
2,3',4,4',5'-PenCB	118	0.5	0.7	0.6	0.5	0.8	0.3	0.5	0.3	0.5	0.2	0.3
2'3,3',4,5'-PenCB	122	<0.02	<0.01	0.01	<0.01	<0.01	<0.01	0.01	<0.01	0.02	<0.01	0.01
2',3,4,4',5'-PenCB	123	<0.02	<0.01	0.01	<0.01	<0.01	<0.01	0.01	<0.01	<0.01	<0.01	0.01
2,2',3,3',4,4'-HexCB	128	0.1	0.3	0.2	0.1	0.1	0.0	0.1	0.1	0.1	<0.01	0.05
2,2',3,4,4',5'-HexCB	138	0.7	2.2	1.6	0.6	0.8	0.3	0.5	0.4	0.5	0.2	0.4
2,2',3,4,5,5'-HexCB	141	0.2	0.8	0.6	0.1	0.2	0.1	0.1	0.1	0.1	0.1	0.1
2,2',3,4',5',6'-HexCB	149	1.0	3.2	2.5	0.9	1.2	0.4	0.8	0.7	0.9	0.4	0.6
2,2',4,4',5,5'-HexCB	153	0.9	3.0	2.3	0.9	1.1	0.4	0.8	0.6	0.8	0.3	0.5
2,3,3',4,4',5'-HexCB	156	0.03	0.2	0.1	0.0	0.1	<0.01	0.03	<0.01	0.0	<0.01	0.0
2,3,3',4,4',5'-HexCB	157	<0.01	<0.01	0.01	<0.01	<0.01	<0.01	0.01	<0.01	<0.01	<0.01	0.0
2,3',4,4',5,5'-HexCB	167	0.02	0.1	0.1	0.01	0.02	<0.01	0.01	0.01	<0.01	<0.01	0.0
2,2',3,3',4,4',5'-HepCB	170	0.1	0.4	0.3	0.04	0.1	<0.01	0.04	0.04	0.1	0.03	0.04
2,2',3,4,4',5,5'-HepCB	180	0.2	1.1	0.8	0.2	0.2	0.1	0.2	0.1	0.2	0.1	0.1
2,2',3,4,4',5',6'-HepCB	183	0.1	0.4	0.3	0.1	0.1	0.03	0.1	0.04	0.1	0.02	0.04
2,2',3,4',5,5',6'-HepCB	187	0.2	0.8	0.6	0.2	0.3	0.1	0.2	0.1	0.2	0.1	0.1
2,3,3',4,4',5,5'-HepCB	189	<0.01	<0.01	0.01	<0.01	<0.01	<0.01	0.01	<0.01	<0.01	<0.01	0.01
2,2',3,3',4,4',5,5'-OctCB	194	<0.01	0.0	0.01	<0.01	<0.01	<0.01	0.01	<0.01	0.01	<0.01	0.01
2,2',3,3',4,4',5,5',6'-NonCB	206	<0.01	<0.01	0.01	<0.01	<0.01	<0.01	0.01	<0.01	0.01	<0.01	0.01
DecaCB	209	<0.01	<0.01	0.01	<0.01	0.03	<0.01	0.01	<0.01	0.02	<0.01	0.01
Sum 7 PCB (PCB28+52+101+118+138+153+180)		10	16	14	9	12	3	8	7	9	3	6
Sum PCB		44	53	50	39	49	16	33	31	42	18	30

Table A 2 Concentration of the all the PAHs in air in the individual samples at Andøya, Bjørnøya and Jan Mayen and the averages for the periods, ng m<sup>-3</sup>.

	Andøya			Bjørnøya				Jan Mayen			
	period 1	period 2	average	period 1	period 2	period 3	average	period 1	period 2	period 3	average
start time	29.11.09	26.02.10	29.11.09	28.08.09	29.12.09	14.04.10	29.12.09	05.10.09	05.01.10	08.04.10	05.01.10
end time	26.02.10	16.08.10	16.08.10	29.12.09	13.04.10	28.08.10	28.08.10	05.01.10	08.04.10	29.07.10	29.07.10
nr of days	89	171	260	123	105	136	364	92	93	112	297
Unit	ng/m3	ng/m3	ng/m3	ng/m3	ng/m3	ng/m3	ng/m3	ng/m3	ng/m3	ng/m3	ng/m3
Fluorene	1.7	0.1	0.7	1.0	0.7	0.1	0.6	1.1	1.0	0.1	0.7
Phenanthrene	1.5	0.3	0.7	0.6	0.7	0.2	0.5	0.3	0.4	0.1	0.3
Anthracene	0.02	<0.01	0.01	0.002	0.002	0.011	0.005	0.002	0.002	0.002	0.002
Fluoranthene	0.44	0.11	0.22	0.19	0.25	0.08	0.17	0.14	0.20	0.03	0.12
Benz(a)anthracene	<0.01	<0.01	0.01	0.002	0.003	0.005	0.003	0.002	0.002	0.001	0.001
Chrysene	0.03	0.01	0.02	0.014	0.029	0.009	0.016	0.012	0.021	0.004	0.012
Benzo(a)pyrene	<0.01	<0.01	0.01	<0.001	0.002	0.001	0.001	0.003	0.002	0.006	0.003
Pyrene	0.12	0.06	0.08	0.05	0.08	0.06	0.06	0.03	0.04	0.01	0.03
<b>Sum 8 PAH</b>	<b>3.8</b>	<b>0.6</b>	<b>1.7</b>	<b>1.9</b>	<b>1.8</b>	<b>0.4</b>	<b>1.3</b>	<b>1.6</b>	<b>1.7</b>	<b>0.2</b>	<b>1.1</b>
Naphtalene	9	3	5	7	3	4	5	17	5	15	12
Benzo(b /j/k )fluoranthenes	0.02	0.03	0.02	0.006	0.024	0.006	0.011	0.031	0.060	0.017	0.035
Benzo(ghi)perylene	<0.01	<0.01	0.01	0.003	0.009	0.003	0.005	0.003	0.001	0.004	0.003
Acenaphthylene	0.02	0.03	0.03	0.01	0.02	0.02	0.02	0.01	0.01	0.02	0.01
Acenaphthene	0.09	0.03	0.05	0.04	0.02	0.03	0.03	0.06	0.04	0.03	0.04
Indeno(1,2,3-cd)pyrene	<0.01	<0.01	0.01	0.001	0.007	0.002	0.003	0.003	0.004	0.001	0.002
Dibenzo(ac/ah)anthracene	<0.01	<0.01	0.01	<0.001	0.005	0.002	0.002	0.003	0.003	0.002	0.002
<b>Sum 16 EPA PAH</b>	<b>13</b>	<b>3</b>	<b>7</b>	<b>9</b>	<b>5</b>	<b>5</b>	<b>6</b>	<b>18</b>	<b>7</b>	<b>15</b>	<b>14</b>
3-Methylphenanthrene	0.06	0.03	0.04	0.05	0.12	0.04	0.07	0.02	0.02	0.01	0.02
2-Methylphenanthrene	0.10	0.04	0.06	0.07	0.16	0.06	0.09	0.03	0.04	0.02	0.03
2-Methylanthracene	<0.01	<0.01	0.01	0.002	0.003	0.002	0.002	0.001	0.001	0.001	0.001
9-Methylphenanthrene	0.04	0.03	0.03	0.04	0.09	0.04	0.05	0.02	0.02	0.01	0.02
1-Methylphenanthrene	0.05	0.03	0.04	0.04	0.08	0.04	0.05	0.02	0.02	0.03	0.02
2-Methylnaphtalene	3.1	0.6	1.4	3.2	2.0	2.6	2.6	3.5	1.5	5.2	3.5
1-Methylnaphtalene	1.8	0.3	0.8	1.7	0.8	1.1	1.2	2.0	0.8	2.3	1.7
Biphenyl	10.8	0.1	3.8	1.3	0.3	0.2	0.6	1.9	0.9	0.7	1.1
Retene	0.04	0.09	0.07	0.08	0.03	0.13	0.08	0.02	0.02	0.12	0.06

Table A 3 Concentration of all the pesticides in air in the individual samples at Andøya, Bjørnøya and Jan Mayen and the averages for the periods,  $\text{pg m}^{-3}$ .

end time	26.02.2010	16.08.2010	16.08.2010	29.12.2009	13.04.2010	28.08.2010	28.08.2010	05.01.2010	08.04.2010	29.07.2010	29.07.2010
nr of days	89	171	260	123	105	136	364	92	93	112	297
Unit	pg/m3	pg/m3	pg/m3	pg/m3	pg/m3	pg/m3	pg/m3	pg/m3	pg/m3	pg/m3	pg/m3
trans-Chlordane	0.7	0.5	0.6	1.1	1.6	0.4	1.0	1.1	1.5	0.6	1.0
cis-Chlordane	1.5	1.4	1.4	2.7	2.9	1.8	2.4	2.4	2.8	1.6	2.2
trans-Nonachlor	1.2	1.2	1.2	2.3	2.5	1.4	2.0	1.9	2.3	1.4	1.9
cis-Nonachlor	<0.09	0.2	0.1	0.2	<0.21	0.3	0.2	0.1	0.2	0.1	0.1
sum 4 chlordaner	3.5	3.2	3.3	6.4	7.0	3.8	5.6	5.6	6.7	3.8	5.2
o,p'-DDE	0.4	0.2	0.3	0.5	0.9	0.2	0.5	0.4	0.7	0.1	0.4
p,p'-DDE	3.3	1.0	1.8	4.7	6.8	2.1	4.3	3.1	3.3	0.6	2.2
o,p'-DDD	0.06	0.05	0.05	0.11	0.14	0.06	0.10	0.09	0.09	0.05	0.08
p,p'-DDD	0.05	0.07	0.06	0.08	0.10	0.05	0.07	0.63	0.06	0.04	0.23
o,p'-DDT	0.7	0.4	0.5	0.9	1.5	0.4	0.9	0.8	1.0	0.3	0.7
p,p'-DDT	0.4	0.3	0.3	0.5	0.9	0.3	0.5	0.4	0.4	0.1	0.3
Sum 6 DDT	4.8	2.0	3.0	6.8	10.3	3.1	6.4	5.4	5.5	1.2	3.9
$\alpha$ -HCH	11.1	12.0	11.7	24.3	21.4	18.6	21.3	22.2	20.4	14.0	18.5
$\gamma$ -HCH	2.4	3.1	2.9	4.1	3.2	2.2	3.1	3.0	3.1	1.8	2.6





## Tilførsler til norske havområder



**KLIMA- OG  
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Utførende institusjon Norsk institutt for vannforskning		ISBN-number 978-82-577-5923-0	
Prosjektleder Norman W. Green		Klifs kontaktperson Christine Daae Olseng	
		TA-number 2808/2011	
		År 2011	Sider 53
		Klif's kontrakt nummer 5011020	
Utgiver Norsk institutt for vannforskning (NIVA), NIVA-rapport 6188-2011		Prosjektet finansiert av Klima- og forurensningsdirektoratet, Klif	
Forfattere Ian J. Allan*, Wenche Aas**, Norman W. Green*, Kine Bæk*, Guttorm Christiansen*** and Knut Breivik**		*Norwegian Institute for Water Research ( NIVA) **Norsk institutt for luftforskning (NILU) ***Akvaplan-niva AS	
Tittel <i>Tilførselsprogrammet 2010. Passive air and water sampling at Andøya, Bjørnøya and Jan Mayen, 2009-2010</i>			
Sammendrag <i>As part of the monitoring programme established by the Climate and Pollution Agency (Klif) to assess fluxes of contaminants in the Barents Sea, Norwegian Sea and North Sea, passive sampling was undertaken at Andøya, Bjørnøya and Jan Mayen to measure levels of polycyclic aromatic hydrocarbons (PAHs), polychlorinated biphenyls (PCBs), organochlorines (OCs) and polybrominated diphenylethers (PBDEs) in air and water. Semipermeable membrane devices and silicone strips were deployed in water for periods of 10-12 months. PAH concentrations in water were low, but mostly quantifiable. PCB concentrations were mostly below limits of detection, despite the latter being in the low picogram/litre range. Limits of detection were adequate for pentachlorobenzene and hexachlorobenzene, while concentrations of hexachlorocyclohexane isomers (-HCH and -HCH) and p,p'-DDE were closer to limits of detection. Two PBDE congeners, PBDE-47 and PBDE-99 were consistently detected. For certain compounds, it was possible to compare dissolved water concentrations with those measured in the whole sediment and accumulated in cod liver. Results from polyurethane foam samplers (PUFs) deployed in the air are broadly consistent with results from past findings and active air samplers, yet also revealed difficulties when applying passive sampling methods in air and water at Arctic sites, which are mainly attributed to the relatively harsh climatic conditions. Contaminant levels in air were successfully measured at the three sites using PUF air samplers. Based on results presented here, some recommendations regarding further work are also provided.</i>			
4 emneord Passive prøvetaking Arktisk overvåking Luft og vann prøvetaking Organiske miljøgifter		4 subject words Passive sampling Arctic monitoring Air and water sampling Organic pollutants	





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## Om Statlig program for forurensningsovervåking

Statlig program for forurensningsovervåking omfatter overvåking av forurensningsforholdene i luft og nedbør, skog, vassdrag, fjorder og havområder. Overvåkingsprogrammet dekker langsiktige undersøkelser av:

- overgjødsling
- forsuring (sur nedbør)
- ozon (ved bakken og i stratosfæren)
- klimagasser
- miljøgifter

Overvåkingsprogrammet skal gi informasjon om tilstanden og utviklingen av forurensningssituasjonen, og påvise eventuell uheldig utvikling på et tidlig tidspunkt. Programmet skal dekke myndighetenes informasjonsbehov om forurensningsforholdene, registrere virkningen av iverksatte tiltak for å redusere forurensningen, og danne grunnlag for vurdering av nye tiltak. Klima- og forurensningsdirektoratet er ansvarlig for gjennomføringen av overvåkingsprogrammet.

SPFO-rapport 1095/2011  
TA 2808/2011