Overvåking av forurensning ved mudring og deponering

Passive prøvetakere rundt dypvannsdeponiet ved Malmøykalven

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Sammendrag

NGI har gjennomført overvåkning med passive prøvetakere i området rundt dypvannsdeponiet ved Malmøykalven i perioden 22/9-06 til 6/11-06. Før nedføringen av mudrede masser ble startet dokumenterte NGI bakgrunnsnivået i området med samme metode.

Bruk av passive prøvetakere gir et tidsintegrert gjennomsnitt av den løste konsentrasjonen av PAH og PCB. Dette er den biotilgjengelige andelen av forbindelsene, dvs. det som kan tas opp av organismer. Metoden gjør det mulig å kvantifisere svært lave konsentrasjoner av PAH og PCB, med nedre bestemmelsesgrense ned mot 0,1-pg/l.

Metoden er dokumentert med omfattende utprøving i laboratorium og en rekke feltforsøk i Oslofjorden.

Oppsummert viser resultatene fra målingene følgende:

- Det ble funnet løst PAH og PCB i området ved undersøkelsene gjort før arbeidene startet opp.
- Det er ikke påvist økning av PAH eller PCB i de øvre vannlag i deponiområdet.
- Det er ingen økning av PAH eller PCB ved målestasjon MP1, MP2 eller MP4 sammenliknet med før arbeidene ble startet.
- Ved MP3 er det ingen økning i PAH eller PCB over 53 m vanndyp.
- Det er ikke observert PAH eller PCB i konsentrasjoner høyere enn grenseverdi for økologisk risiko, med unntak av PCB-118 i bunnvannet ved MP3.
- Ved målestasjon MP3 er det observert forhøyede konsentrasjoner av PCB og PAH i bunnvannet (63 m dyp) sammenliknet med før-situasjonen. Konsentrasjonen av stoffene er lavere enn det som er beregnet i konsekvensutredningen.

Innhold

Vedlegg A	Resultater passive prøvetakere
Vedlegg B	Cornelissen et. al. (submitted). “Equilibrium passive samplers to determine freely dissolved native PAH concentrations in field and laboratory”

Kontroll- og referanseside

1 INNLEDNING

NGI utfører på vegne av Oslo Havn KF overvåkning av mudring av forurensede havnesedimenter og deponering av disse massene i dypvannsdeponi ved Malmøykalven.

Arbeidene er underlagt omfattende krav til overvåkning og dokumentasjon i tillatelser gitt av SFT. Disse kravene er beskrevet i kontrollplanen for arbeidene.

I tillegg til den pålagte overvåkningen har Oslo Havn KF tatt initiativ til et utvidet måleprogram som omfatter bruk av passive prøvetakere. Denne rapporten presenterer gjennomføring og resultater fra en undersøkelse med passive prøvetakere utplassert rundt dypvannsdeponiet ved Malmøykalven i perioden 22/9-06 til 6/11-06.

2 BAKGRUNN

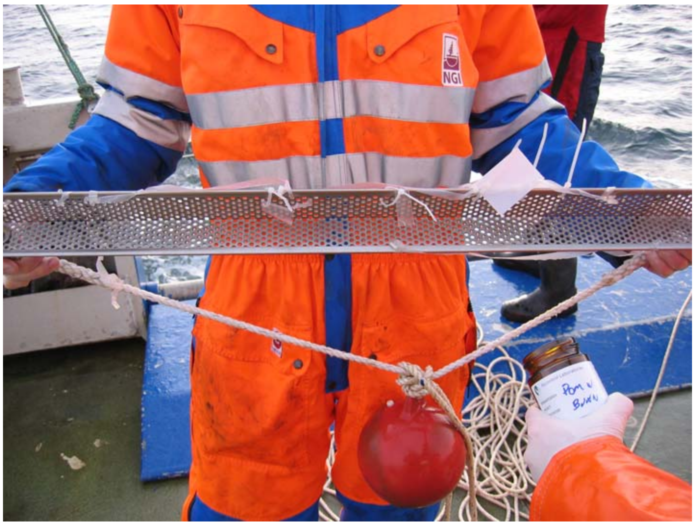
Det er benyttet passive prøvetakere i overvåkningen av arbeidene med nedføring av mudrede masser til dypvannsdeponiet ved Malmøykalven for å komplettere bruk av stikkprøver for dokumentasjon av vannkvalitet.

- Metoden omfatter analyse av hydrofobe organiske forbindelser som PAH og PCB.
- Det oppnås en tidsintegrert, gjennomsnittlig konsentrasjon av analyserte løste forbindelser. Dette tilsvarer den biotilgjengelige andelen av forbindelsene. Dette er en mer relevant måling enn analyse av totalinnhold (med partikler) når det skal vurderes opptak i organismer.
- Metoden kvantifiserer forbindelser i svært lave konsentrasjoner.

Metodens virkemåte er at det plasseres ut passive prøvetakere i en oppankret bøyerigg slik at prøvetakeren henger på kjente nivåer nedover i vannsøylen. Utstyret blir stående ute til det oppnådd en likevekt mellom de vannløste organiske forbindelser (PAH og PCB). Likevektsfordelingen (likevektskonstanten) mellom forbindelsene i prøvetakeren og vannfasen er kjent. Etter at likevekt er oppnådd hentes prøvetakerne inn og analyseres på høytoppløsende gasskromatograf (GC-MS). Resultatene blir omregnet til konsentrasjonen av fritt løst PAH og PCB i vann.

3 FELTARBEID

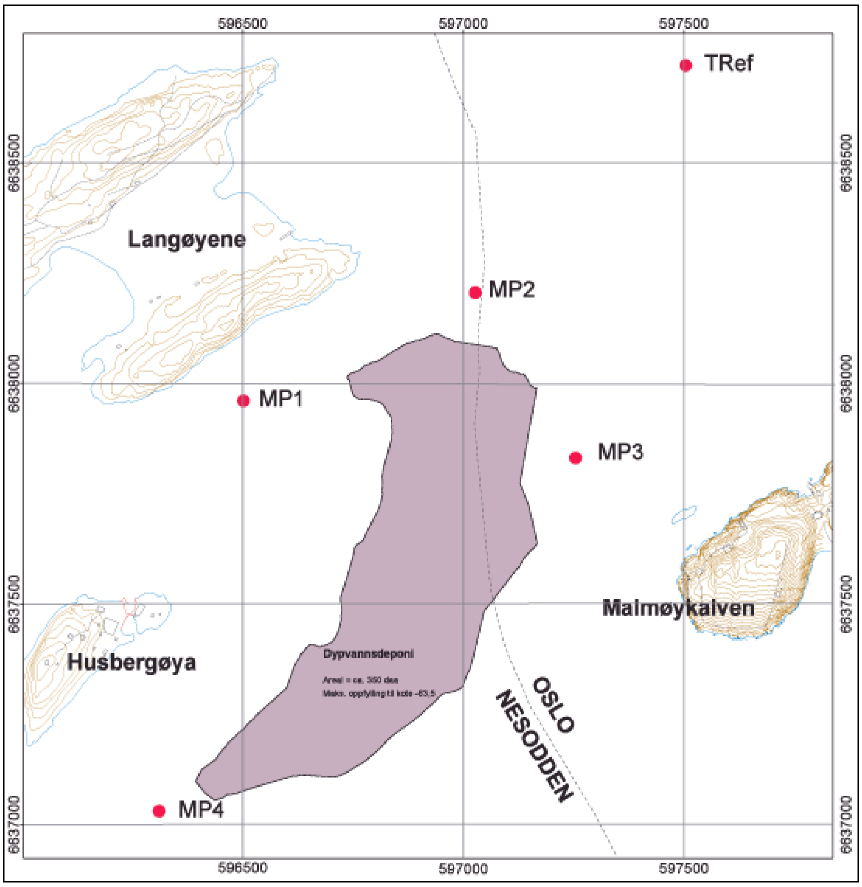
De passive prøvetakerne består av polyoxymethylen (POM) og er utført i tynne strimler med tykkelse 55 µm. Disse når likevekt i felt etter 3-6 uker. Hver enkelt måling er gjort i opp til tre uavhengige paralleller, dvs. tre passive prøvetakere er satt ut i alle nivåer og de er analysert hver for seg. Dette gir et godt statistisk grunnlag og sikrer at måleusikkerhet basert på reproduserbarhet inngår ved vurdering av endringer og forskjeller i måleverdier. Fotografiet i figur 1 viser passive prøvetakere rigget opp i overvåkningsbøye.



Figur 1 Foto av passive prøvetakere i bøyerigg

NGI utplasserte passive prøvetakere rundt deponiet 22/9-06. Disse ble hentet inn 6/11-06. Det ble utplassert passive prøvetakere ved overvåkningsbøye MP1, MP2, MP3, MP4 og Tref. Se figur 2 for oversiktskart. Det er satt ut prøvetakere i flere nivåer nedover i vannsøylen, se tabell 1.

Det ble også utplassert to overvåkningsrigger med passive prøvetakere i deponiområdet før arbeidene med nedføring ble startet. Disse riggene hadde, som det framgår av tabell 1, passive prøvetakere i to nivåer (5 m vanndyp og 5 m over sjøbunn). Resultatene fra disse målingene angir bakgrunnsnivået i området.



Figur 2 *Kart over deponiområdet med målestasjoner for passive prøvetakere*

Tabell 1 *Dybdenivåer for passive prøvetakere*

Stasjon	Vanndyp (m)	Tidsperiode	Antall replikater
POM S	3m vanndyp og 5 m over sjøbunn	15/12-05 til 24/1-06* (40 dager)	2
POM N	3m vanndyp og 5 m over sjøbunn		
MP1	3m vanndyp og 5 m over sjøbunn	22/9-06 til 6/11-06 (45 dager)	3
MP2	3m vanndyp og 5 m over sjøbunn		3
MP3	3m, 13m 23m, 33m, 43m, 53m, 63m		1-2
MP4	3m, 15m, 27m, 39m, 51m, 63m		1-2
Tref	3m vanndyp og 5 m over sjøbunn		3

*før arbeidene med nedføring av mudrede masser var startet

4 ANALYSER

Kjemisk analyse av passive prøvetakere ble utført ved NGI Miljølaboratoriet Laboratoriet er akkreditert iht. NS-EN ISO/IEC 17025. Det ble benyttet Agilent 6850 gasskromatograf med 5973 massespektrometer (GC-MS).

Ekstraksjon og opparbeiding av de passive prøvetakerne er utført ved å tilsette heksan og intern standard og plassere dette på ristebord i 96 timer. Organisk ekstrakt ble separert ut og konsentrasjonen av PAH og PCB ble kvantifisert med GC-MS etter opprensking med silikagel. Kromatogrammene viser at det oppnås god grunnlinjeseparasjon og at metoden har god følsomhet.

4.1 Validering av metoden

NGI har testet optimert og verifisert metode for bruk av passive prøvetakere. Dette arbeidet ble startet høsten 2005, og har omfattet validering i laboratorium og felt. Det er blitt utplassert flere typer passive prøvetakere ved dypvannsdeponiet, Kongshavn og i Bispevika. Forsøkene omfatter dokumentasjon av metodens reproduserbarhet, måleusikkerhet, nedre bestemmelsesgrense og nøyaktighet. Testene viser at passive prøvetakere av polyoxymetylen er svært egnet til formålet. Det er utarbeidet stoffspesifikke likevektskonstanter for omregning til konsentrasjon av PAH og PCB løst i vann. Metodens nedre bestemmelsesgrense er 0,1 til 1 pg/l avhengig av enkeltkomponentenes molekylstørrelse. Det er utviklet bøyeoppsett for utplassering og funnet optimal tidslengde for utplassering.
Dette arbeidet er sammenfattet i vitenskapelig artikkel (Cornelissen et. al., submitted) som er gjengitt i sin helhet i vedlegg B.

5 RESULTATER

Resultatene er presentert i sin helhet i tabell 1 og 2 i vedlegg A. PAH omfatter kvantifisering av 14 enkeltkongenere, PCB omfatter 11 kongenerer.

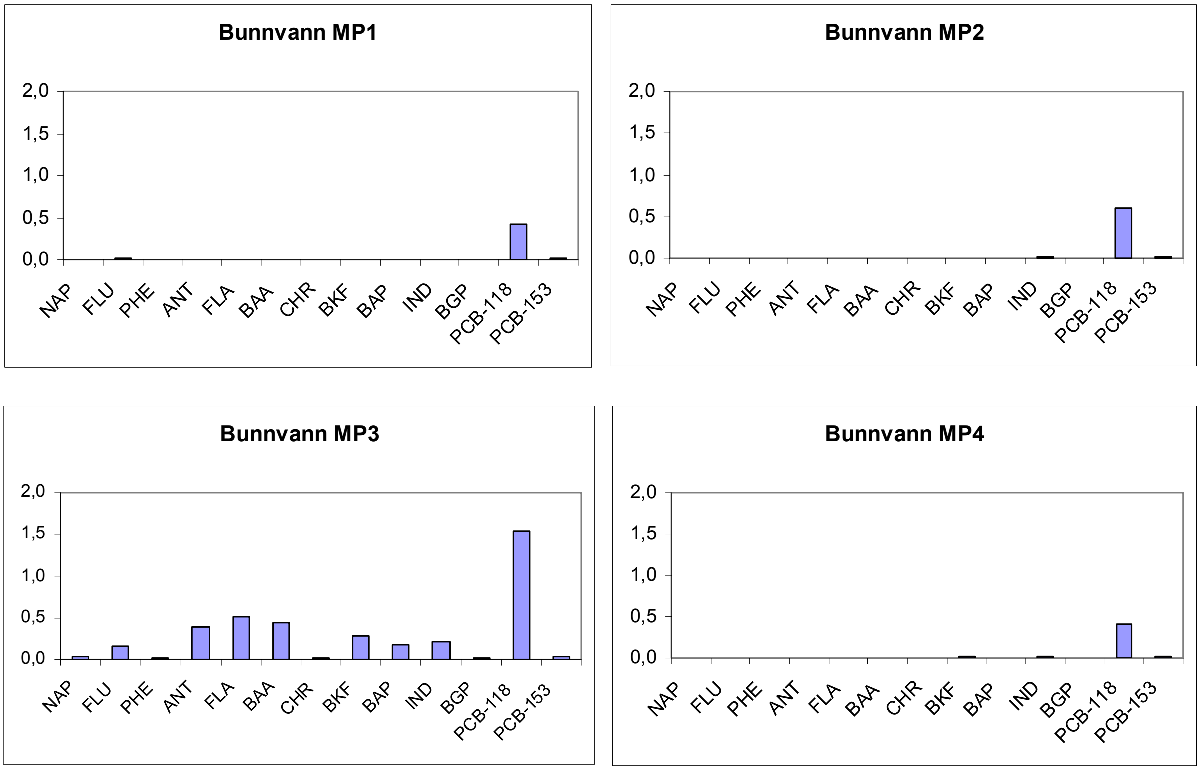
Resultatene viser at det før arbeidene med nedføring av masser til dypvannsdeponiet startet ble observert PAH og PCB både i overflatevann og i bunnvannet i deponiet. Etter at arbeidene har pågått 8 måneder viste målingene at det ved målestasjon MP1, MP2 og MP4 ikke er noen signifikant forskjell i nivåene av løst PAH og PCB i vannet fra overflaten og ned til sjøbunnen. Ved målestasjon MP3 er det ingen endring fra overflaten og ned til ca. 53 m vanndyp. Ved 60 m vanndyp har konsentrasjonen av PAH og PCB forbindelser økt i forhold til det som ble målt før start av nedføring.

Tabell 2 viser nivåene av PAH og PCB sammenliknet med målinger fra før-situasjonen. Resultatet fra målingen av førsituasjonen er satt til 1. desember 2006. Der forholdet er gitt til 1 betyr dette at det ikke er forskjell i konsentrasjonen av PAH eller PCB sammenliknet med før-situasjonen. Er forholdstallet lavere enn 1 er observert konsentrasjon nå lavere, og der forholdstallet er høyere enn 1 er observert konsentrasjon høyere enn i før-situasjonen.

Tabell 2 Relativ endring i PAH og PCB i forhold til før-situasjonen, som er satt til 1

Målestasjon	Vanndyp (m)	PAH	PCB
T ref	5	2,2	1,0
T ref	5 m over sjøbunn	3,2	0,9
MP1	5	0,8	0,5
MP1	5 m over sjøbunn	0,9	0,8
MP2	5	1,1	0,6
MP2	5 m over sjøbunn	0,8	0,6
MP3	13	0,9	0,8
MP3	23	0,8	0,8
MP3	33	0,8	0,9
MP3	43	1,2	0,9
MP3	53	3,1	0,9
MP3	63	37,5	2,9
MP4	3	0,7	0,4
MP4	15	0,5	0,5
MP4	27	0,6	0,7
MP4	39	0,3	0,4
MP4	51	0,4	0,4
MP4	63	0,8	0,4

I tabellene i vedlegg A er det vist grenseverdi for økologisk risiko (HC5). Dette er konsentrasjonen som beskytter 95 % av organismene. HC5 verdiene er hentet fra SFT (2005). Som det framgår av tabell 2 og 3 er det ikke observert PAH eller PCB over HC5 i noen av prøvene, bortsett fra en av PCB kongenerene (PCB 118) foreligger i konsentrasjon bunnvannet (63 m vanndyp) ved målestasjon MP3. Figur 3 illustrerer observerte konsentrasjoner av PAH og PCB i forhold til grenseverdi for økologisk risiko (HC5). Når forholdet er lavere enn 1 er grenseverdi ikke overskredet.

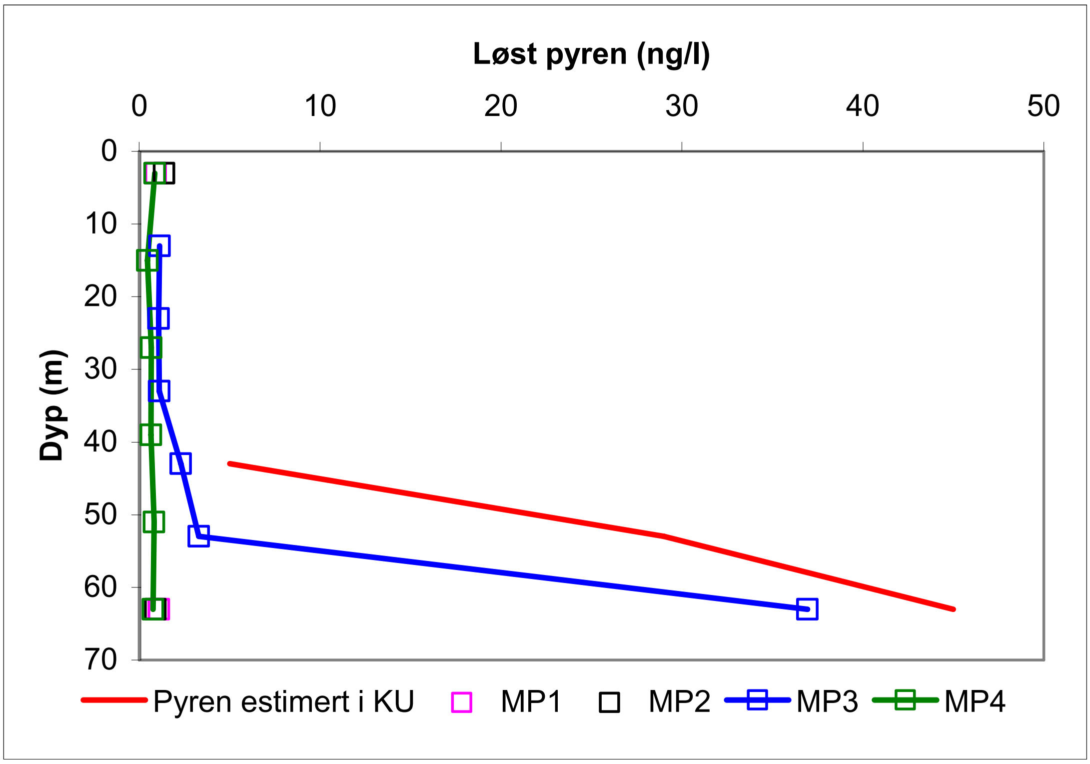


Figur 3 *Forholdet mellom observerte konsentrasjoner av PAH og PCB forbindelser i bunnvannet ved målestasjon MP1, MP2, MP3 og MP4 sammenliknet med grenseverdi for økologisk risiko*

6 VURDERING OG KONKLUSJON

Bruk av passive prøvetakere gjør det mulig å detektere svært lave konsentrasjoner av løst PAH og PCB i vann. Resultatene representerer et tidsintegrert gjennomsnitt for den perioden prøvetakerne har vært utplassert.

Ved utarbeidelse av konsekvensutredning for tiltaket (Oslo kommune, 2001 og NGI/NIVA, 2003) er det utarbeidet miljøbudsjett for tiltaket. Det er beregnet miljøgevinst som oppnås og estimert spredning av ulike metaller og organiske forbindelser som følge av sjøarbeidene. I konsekvensutredningen er det modellert spredning av ulike forbindelser i bunnvannet i Bekkelagsbassenget som følge av nedføring av mudrede masser. I figur 4 er estimert konsentrasjon av PAH komponenten pyren plottet sammen med observerte konsentrasjoner ved målestasjon MP1, MP2, MP3 og MP4. Figuren viser at alle observerte konsentrasjoner av pyren er under nivået som er beregnet i konsekvensutredningen.



Figur 4 *Målt konsentrasjon av pyren ved målestasjonene MP1, MP2, MP3 og MP4 sammenliknet med estimert konsentrasjon fra konsekvensutredningen (KU)*

7 OPPSUMMERING

NGI har gjennomført målinger med passive prøvetakere ved overvåkningsstasjonene MP1, MP2, MP3, MP4 og Tref ved dypvannsdeponiet. Denne metoden gir et tidsintegrert gjennomsnitt av konsentrasjonen av løst PAH og PCB i vann, og metoden gjør det mulig å måle svært lave konsentrasjoner av disse forbindelsene (nedre bestemmelsesgrense ned mot 0,1-1 pg/l).
Resultatene fra undersøkelsen i perioden september til november 2006 viser at:

- Det ble funnet løst PAH og PCB i området ved undersøkelsene gjort før arbeidene startet opp.
- Det er ikke påvist økning av PAH eller PCB i de øvre vannlag i deponiområdet.
- Det er ingen økning av PAH eller PCB ved målestasjon MP1, MP2 eller MP4 sammenliknet med før arbeidene ble startet.
- Ved MP3 er det ingen økning i PAH eller PCB over 53 m vanndyp.
- Det er ikke observert PAH eller PCB i konsentrasjoner høyere enn grenseverdi for økologisk risiko, med unntak av PCB-118 i bunnvannet ved MP3.

- Ved målestasjon MP3 er det observert forhøyede konsentrasjoner av PCB og PAH i bunnvannet (63 m dyp) sammenliknet med før-situasjonen. Konsentrasjonen av stoffene er lavere enn det som er beregnet i konsekvensutredningen.

8 REFERANSER

NGI/NIVA (2003)
Oslo Havnevesen. Dypvannsdeponi ved Malmøykalven. Tilleggsutredning til konsekvensutredning. Miljøbudsjett, kostnader og in situ tildekking. NGI rapport 20011067-1, datert 2. januar 2001.

Oslo kommune (2001)
Konsekvensutredning. Dypvannsdeponi for forurenset bunnsediment ved Malmøykalve, Oslo havnedistrikt. Oktober 2001

SFT (2005)
Veileder for forurenset sediment. SFT TA-2085/2005, ISBN 82-7655-250-1

Vedlegg A - Resultater fra passive prøvetakere

INNHOLD

9 RESULTATER PAH

Tabell 1 Konsentrasjonen (ng/l) av enkeltkongenerer fritt løst PAH

Stasjon	Dyp (m)	NAP	FLU	PHE	ANT	FLA	PYR	BAA	CHR	BBF	BKF	BEP	BAP	IND	BGP
*POM S	5	32,20	0,50	1,75	0,11	1,06	1,45	0,07	0,33	0,08	0,06	0,06	0,03	0,008	0,007
*POM S	bunn	88,72	0,39	1,44	0,11	0,54	1,19	0,03	0,11	0,03	0,02	0,03	0,02	0,005	0,005
*POM N	5	43,32	0,56	2,48	0,12	1,22	1,57	0,06	0,30	0,09	0,06	0,07	0,04	0,012	0,011
*POM N	bunn	53,61	0,34	1,36	0,14	0,56	1,05	0,03	0,10	0,03	0,02	0,03	0,02	0,005	0,006
T ref	5	3,97	5,79	1,92	0,64	1,92	1,53	0,09	0,26	0,05	0,05	0,03	0,02	0,005	0,004
T ref	bunn	5,89	1,07	1,45	0,39	4,12	2,20	0,30	0,79	0,22	0,13	0,14	0,15	0,027	0,017
MP1	5	2,91	0,82	1,47	0,10	1,24	0,92	0,07	0,21	0,03	0,04	0,02	0,02	0,004	0,003
MP1	bunn	6,99	2,00	2,28	0,21	0,40	1,09	0,01	0,07	0,02	0,01	0,02	0,01	0,004	0,003
MP2	5	7,19	0,62	1,35	0,11	1,85	1,37	0,10	0,30	0,05	0,06	0,04	0,02	0,005	0,004
MP2	bunn	7,96	0,74	0,73	0,10	0,92	0,90	0,05	0,19	0,04	0,03	0,04	0,03	0,006	0,004
MP3	13	3,31	0,66	1,16	0,05	0,87	1,14	0,03	0,17	0,05	0,03	0,04	0,02	0,010	0,010
MP3	23	3,30	0,69	1,14	0,06	0,83	1,08	0,03	0,15	0,04	0,03	0,03	0,02	0,009	0,008
MP3	33	3,98	0,69	1,20	0,07	0,86	1,11	0,03	0,16	0,04	0,03	0,03	0,02	0,008	0,008
MP3	43	7,21	2,05	2,83	0,06	0,78	2,30	0,03	0,19	0,06	0,03	0,04	0,03	0,009	0,008
MP3	53	8,99	3,67	3,15	0,26	2,59	3,29	0,16	0,64	0,16	0,10	0,14	0,12	0,027	0,020
MP3	63	66,71	19,49	35,59	13,15	61,72	36,94	4,36	6,93	1,26	1,04	0,65	0,90	0,126	0,076
MP4	3	1,59	0,60	1,05	0,10	1,15	0,86	0,07	0,18	0,04	0,03	0,02	0,02	0,003	0,002
MP4	15	2,82	0,51	0,83	0,06	0,31	0,45	0,02	0,07	0,03	0,02	0,02	0,01	0,004	0,003
MP4	27	5,66	0,58	0,61	0,32	0,30	0,67	0,01	0,06	0,02	0,01	0,01	0,01	0,004	0,003
MP4	39	8,42	0,23	0,43	0,01	0,23	0,65	0,01	0,07	0,02	0,01	0,01	0,01	0,003	0,003
MP4	51	8,22	0,20	0,29	0,02	0,26	0,83	0,05	0,01	0,02	0,01	0,02	0,01	0,003	0,002
MP4	63	7,72	0,32	0,38	0,06	0,52	0,77	0,05	0,17	0,05	0,03	0,04	0,04	0,009	0,007
HC5**		2100	120	3200	34	120		10	280		3,6		5	0,61	3,1

*Før-situasjon målt i perioden 15/12-05 til 24/1-06

**Grenseverdi for økologisk risiko (SFT, 2005)

Bunn er nivå 5 m over sjøbunnen

NAP = naphthalene, FLU = fluorene, PHE = phenanthrene, ANT = anthracene, FLA = fluoranthene, PYR = pyrene, BAA = benz[a]anthracene, CHR = chrysene, BBF = benzo[b]fluoranthene, BKF = benzo[k]fluoranthene, BEP = benzo[e]pyrene, BAP = benzo[a]pyrene, IND = indeno[1,2,3-cd]pyrene, BGP = benzo[ghi]perylene.

10 RESULTATER PCB

Tabell 2 Konsentrasjonen (ng/l) av enkeltkongenerer fritt løst PCB

Stasjon	**Dyp (m)**	**PCB-28**	**PCB-52**	**PCB-70**	**PCB-101**	**PCB-110**	**PCB-118**	**PCB-105**	**PCB-149**	**PCB-153**	**PCB-138**	**PCB-180**	**ΣPCB-7**
*POM S	5	0,027	0,016	0,010	0,009	0,012	0,008	0,004	0,003	0,005	0,007	0,0006	0,072
*POM S	bunn	0,031	0,019	0,013	0,006	0,010	0,005	0,002	0,003	0,004	0,005	0,0006	0,069
*POM N	5	0,027	0,017	0,016	0,009	0,013	0,007	0,003	0,003	0,006	0,008	0,0006	0,074
*POM N	bunn	0,026	0,016	0,012	0,007	0,010	0,006	0,004	0,003	0,004	0,006	0,0004	0,066
T ref	5	0,038	0,020	0,016	0,005	0,006	0,003	0,002	0,001	0,002	0,002		0,071
T ref	bunn	0,019	0,014	0,013	0,008	0,016	0,010	0,005	0,003	0,005	0,007	0,0002	0,065
												0,0005	
MP1	5	0,014	0,010	0,009	0,005	0,005	0,003	0,002	0,001	0,002	0,002		0,037
MP1	bunn	0,024	0,016	0,011	0,005	0,007	0,005	0,002	0,001	0,003	0,004	0,0002	0,058
												0,0003	
MP2	5	0,016	0,012	0,010	0,005	0,005	0,004	0,002	0,001	0,002	0,003		0,042
MP2	bunn	0,012	0,011	0,007	0,006	0,009	0,007	0,003	0,002	0,004	0,005	0,0001	0,044
												0,0003	
MP3	13	0,019	0,018	0,015	0,007	0,009	0,007	0,003	0,002	0,004	0,005		0,059
MP3	23	0,019	0,017	0,014	0,008	0,009	0,006	0,003	0,002	0,003	0,005	0,0003	0,059
MP3	33	0,021	0,019	0,015	0,008	0,010	0,007	0,004	0,002	0,003	0,005	0,0003	0,064
MP3	43	0,026	0,017	0,014	0,005	0,007	0,007	0,004	0,002	0,003	0,005	0,0004	0,064
MP3	53	0,021	0,018	0,012	0,007	0,014	0,008	0,005	0,002	0,004	0,006	0,0004	0,065
MP3	63	0,069	0,070	0,048	0,024	0,030	0,017	0,008	0,005	0,009	0,011	0,0005	0,202
												0,0010	
MP4	3	0,011	0,008	0,009	0,004	0,004	0,003	0,002	0,001	0,002	0,002		0,030
MP4	15	0,011	0,010	0,010	0,005	0,006	0,005	0,002	0,001	0,003	0,004	0,0002	0,038
MP4	27	0,020	0,012	0,009	0,005	0,005	0,004	0,002	0,001	0,003	0,003	0,0003	0,047
MP4	39	0,009	0,007	0,006	0,004	0,005	0,004	0,002	0,001	0,002	0,003	0,0002	0,029
MP4	51	0,009	0,007	0,010	0,004	0,006	0,004	0,002	0,001	0,003	0,004	0,0002	0,030
MP4	63	0,007	0,007	0,006	0,004	0,007	0,005	0,002	0,001	0,003	0,004	0,0003	0,030
HC5**							0,0111			0,204			

*Før-situasjon målt i perioden 15/12-05 til 24/1-06
**Grenseverdi for økologisk risiko (SFT, 2005)
Bunn er nivå 5 m over sjøbunnen

Vedlegg B - Cornelissen et. al. Submitted

Equilibrium passive samplers to determine freely dissolved native PAH concentrations in field and laboratory

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Abstract

There is a dire need for reliable methods to determine freely dissolved concentrations ($C_{W,free}$) of hydrophobic organic compounds, as $C_{W,free}$ is much better related to bioaccumulation than total sediment contents. Equilibrium passive samplers are promising tools for such measurements. However, up till now the use of equilibrium passive samplers in the field has remained a challenge. In the current study on native PAHs in sediment at four stations in Oslo Harbor, Norway, i) different passive sampler materials were used to laboratory-determine $C_{W,free}$ in porewater, ii) for the determination of $C_{W,free}$ in overlying water, it was tested which passive sampler was most suitable under field conditions, and iii) chemical activity ratios between sediment and overlying water were determined. For laboratory determinations of $C_{W,free}$ in porewater, both 55-µm thick polyoxymethylene (POM-55) and 200-µm thick polydimethylsiloxane (PDMS) tubing turned out to be suited. In the field, shortest equilibrium times (around one month) were observed for POM-55 and 28-µm thick PDMS-coatings on solid-phase micro-extraction (SPME) fibers, with PDMS tubing as a good alternative. Low-density polyethylene of 100-µm thickness (LDPE) and 500-µm thick POM did not reach equilibrium within 119 d in the field. Realistic values were obtained for DOC-to-water distribution ratios in the field (about one log-unit under log K_{OW}), which strengthened the conclusion that equilibrium was established in field-exposed passive samplers. At all four stations chemical activity ratios between porewater and overlying water were over one for all PAHs, indicating that the sediment is a PAH diffusion source and that sediment remediation is potentially useful for PAH contamination in Oslo harbor.

Introduction

In most countries, existing sediment quality criteria for organic compounds are still based on total solid-phase concentrations. However, numerous studies have now demonstrated that these total contents bear little or no relation to actual concentrations observed in organisms. This discrepancy is due to the fact that biota-to-sediment accumulation factors (BSAFs) vary as a result of strong sorption to carbonaceous materials such as soot, charcoal, coal and kerogen [1-3]. In contrast to total sediment contents, freely dissolved porewater concentrations ($C_{W,free}$, closely linked to chemical activities) are related to concentrations in organisms. Therefore ecotoxicological risk assessment should be based on $C_{W,free}$ [2-8].

Nowadays $C_{W,free}$ in sediment porewater can be determined in the laboratory through equilibrium solid-phase extractions of sediment slurries with passive samplers such as polydimethylsiloxane (PDMS) coatings on glass fibers (Solid-Phase Micro-Extraction, SPME) [6,8-15], PDMS sheets [16], polyoxymethylene (POM) strips [17,18], low-density polyethylene (LDPE) sheets [19-21], or ethylene vinyl acetate coatings (EVA) [22], where $C_{W,free}$ is inferred from the uptake in these polymers.

However, up till now the use of equilibrium passive samplers in the field has remained a challenge. Field deployment is a necessity for the measurement of $C_{W,free}$ of hydrophobic compounds in the water column. Often semi-permeable membrane devices (SPMDs) have been used, but these have the disadvantage that they do not reach equilibrium with the surrounding water [23,24] so that either diffusion calculations [23,24] or isotopically labeled internal standards ("performance reference compounds") [16,24] are needed to correct for incomplete equilibration. Equilibrium passive samplers have only been field-tested in a limited number of occasions. In a study by Booij et al. [19], 70-μm thick LDPE was used in the field. It was concluded that diffusion kinetics calculations were necessary for the field situation to deduce the $C_{W,free}$ from the amounts taken up by the passive samplers, although the samplers reached equilibrium in the laboratory within 1-60 d for PAHs in shaken sediment slurries. The relatively long equilibration times in the field can probably be explained by the more stagnant conditions and the high LDPE-to-water distribution ratios that are approximately equal to K_{OW} [19] and thus 10-50 times higher than for e.g. POM [17,18]. High polymer-to-water distribution ratios imply that a large volume of water needs to sampled, and thus a large amount of compound has to pass the diffusive boundary layer adjacent to the polymer surface.

The present study focused on three aims. The first aim was to compare different equilibrium passive samplers to measure $C_{W,free}$ of native PAHs in the laboratory. The agreement or disagreement between such independent measurements will give valuable novel information about the samplers' reliability. The second aim was to find which passive sampler would be most suited for the field determination of $C_{W,free}$ for PAHs in overlying water. This is the first study to compare various equilibrium passive samplers under field conditions. We tested LDPE as well as a number of less strongly sorbing passive sampler materials of variable thicknesses (POM, PDMS). Tests were carried out at four stations in Oslo Harbor. The third aim was to determine the chemical activity ratio between sediment and overlying water. This ratio determines the direction and extent of the PAH diffusion flux at the sediment-water interface. Such flux estimates are a key parameter to access the potential beneficial effect of remedial actions for contaminated sediments.

Materials and Methods

Materials. Additive-free polymer materials were used, including medical-grade PDMS silicon tubing (core diameter 750 µm, thickness 200 µm) from A-M systems, Inc (Carlsborg, WA, USA), PDMS fibers used for SPME (110 µm core diameter, 28.5 µm thick PDMS coating, i.e. 12.4 µL/m) from Poly Micro Industries (Phoenix, AZ, USA), LDPE (thickness 100 µm) from Exposmeter (Sweden), POM of 500 µm thickness (POM-500) from Vink Kunststoffen BV (The Netherlands) and POM of 55 µm thickness (POM-55, obtained in ~1-kg cylinder-shaped blocks and sliced on a lathe equipped with a high-precision razor blade) from Astrup AS (Norway). Both POM-55 and POM-500 consisted of C-POM, which is a copolymer of $(CH_2O)_n$ produced from trioxane and other monomers.

LDPE and POM were pre-cleaned by washing in hexane and methanol followed by drying overnight at 60°C. PDMS tubing was washed in ethylacetate and dried in the same manner. SPME fibers were pre-cleaned by heating overnight at 275°C. All solvents were of glass-distilled quality.

Sampling locations. Native PAHs were studied at four locations in the harbor of Oslo, Norway (Table 1): three heavily contaminated locations in the Inner Harbor (R6, Q8 and PAH "hotspot" O10) and one moderately contaminated site in the Outer Harbor (NR). The inner and outer harbor stations were approximately 1.5 km apart. The inner harbor stations were located less than 100 m from each other. Surface sediment was obtained at all stations using a Van Veen grab corer to carefully sample the 0-5 cm top layer.

Field studies on $C_{W,free}$ in overlying water as well as laboratory determinations of $C_{W,free}$ in porewater were conducted for native PAHs at all four stations. The following experiments were only performed for station NR: i) exposure time series to test passive sampler equilibration rates in the field and in the laboratory, ii) total solvent extraction of the overlying water to compare total dissolved aqueous concentrations ($C_{W,total}$) with $C_{W,free}$-values determined with passive samplers.

Sediment characterization. Total organic carbon (TOC) contents were determined with catalytic combustion elemental analysis at 1030 °C after micro-acidification (2–4 times 30 µl of 1 M HCl for

10-mg samples). Black carbon (BC) contents were determined using the same method on samples combusted at 375 ^{o}C for 18 h under abundant oxygen access to create a material with only BC and no other organic carbon.

Laboratory studies

All laboratory studies were carried out in triplicate, at 20 ± 1°C, in 50-mL all-glass flasks, in the presence of 100 mg NaN_3 (biocide) and NaCl (1.5 g, i.e. 3%, providing a constant ionic strength comparable to the *in situ* conditions at the sampling sites), and shaken end-over-end (6 rpm). Internal standard was 40 ng d_{10}-phenanthrene (d_{10}-PHE, >98% purity) in both laboratory and field studies.

Passive sampler calibration. Passive sampler-water distribution ratios were measured without sediment by shaking PAH stock solution (50 mL) and passive sampler (1-2 mg for PDMS-SPME fibers, 5-25 mg for the other samplers) for 119 d. After equilibration, the passive samplers were removed from the system and dried. The aqueous phase was moved to a clean glass flask and extracted with 10 mL hexane with internal standard. The passive samplers (including the SPME fibers) were extracted by horizontal shaking (230 rpm; 96 h) with hexane (10 mL) with internal standard. The extraction efficiency of this procedure was checked by adding a fresh 10 mL of hexane to the already extracted passive samplers and shaking for additional 10 days; the amounts extracted in this second round were < 3% of the amounts extracted by the first 10 mL of hexane. For POM, PDMS-SPME and LDPE, linear sorption has previously been verified [8,9,17,18,19]. Thus, we verified this only for PDMS tubing. To this end, the abovementioned calibration experiments were conducted for PDMS tubing at six different PAH concentrations spanning a two-orders of magnitude concentration range.

Because temperatures in the field were variable and below room temperature during the exposure period (Table 1), we also measured passive sampler-water distribution ratios at 8 ± 1 °C for POM-500 and PDMS sheet, in the same manner as described above.

Sediment porewater contents and K_{TOC}. Native PAHs were exhaustively extracted from the sediment phases (n=12) by hexane (40 mL)-acetone (10 mL) reflux (6 h) as described in [18]. Passive sampler laboratory experiments were only carried out with POM-55, POM-500 and PDMS tubing. Double triplicate sets of passive sampler (50-200 mg for all materials), sediment (1.5-2 g dry weight), and distilled water (50 mL) were shaken end-over-end as described above for 10 d (triplicates) and 30 d (triplicates). No PAHs were spiked as we studied native compounds present in the sediments. After equilibration, the passive sampler strips were extracted as described above. One can deduce $C_{W,free}$ from the sorbate contents in the samplers with concentration-independent sampler-water distribution ratios that are specific for the various passive sampler materials. A slight depletion of the PAHs in the sediment phase is expected to occur during these experiments; it turned out that 0.1-5% of the total PAH amounts in the solid phase was transferred to the passive samplers during equilibration. This depletion was corrected for by multiplying the determined $C_{W,free}$-values with $(1+f_{depl})$, where f_{depl} is the measured fraction of PAH that was transferred from sediment to passive sampler.

PAH quantification. Hexane extracts were cleaned-up by shaking overnight with activated Cu, passage through a silica column, and drying with Na_2SO_4. The quantification of 14 PAHs was done on a GC-MS (Agilent 6850 GC coupled to 5973 MS in electron impact mode). We chose to report sorption coefficients for a saline system, and not correct the sorption coefficients for the "salt effect" caused by the NaCl concentration [25].

Field studies

Passive sampler materials (all five materials) were attached to 1-m wide triangular Al frames that were held at 50 cm above the sediment by buoys. The whole systems were moored to the bottom by 15-kg weights. The systems could easily be retrieved and sampled via ropes that were anchored to the shore. Care was taken to place the systems back at accurately the same position (within 5-10 m) after sampling. After 23, 63, 97 and 119 days, triplicate samples of each passive sampler were taken from the frames (amounts per individual sample: 0.2-0.5 g POM-55, 2.0-2.4 g POM-500, 0.1-0.2 g LDPE, 20-30 cm SPME fiber i.e. 3-5 mg PDMS coating, 0.1-0.3 g PDMS tubing). In addition, triplicate 5-L water samples were also taken from 50 cm above the bottom, at the beginning of the equilibration time as well as at each sampling time. Water samples were extracted immediately with 2 x 20 mL hexane after addition of internal standard. In addition, 15-mL water samples were taken in Falcon tubes (VWR International, Norway), acidified directly by adding 300 µL 1 M HCl, and sent for TOC analysis of the water phase (particulate plus dissolved OC, POC + DOC) at Umeå University, Sweden.

The passive samplers were cleaned, extracted and analyzed for PAHs as described above. In all cases, biofouling of the polymer materials was so limited that thorough wiping with a paper tissue sufficed to obtain visibly clean materials.

Results and discussion

Passive sampler calibration. Passive sampler-to-water distribution ratios K were 0.2-1.5 log-unit below K_{OW} (Table 2 for PYR and BAP, Table SI-1 for all PAHs). LDPE was the most strongly sorbing material, probably because of the absence of polar atoms and its low degree of crosslinking. $K_{POM\text{-}500}$, K_{LDPE}, $K_{PDMS\text{-}SPME}$ and $K_{PDMS\text{-}tubing}$ were in the range of earlier reported values (Table 2 and references therein). The PDMS tubing material fulfilled the criterion of linear sorption over a wide concentration range (Figure 1). Surprisingly, there was a difference (0.01-0.39 log-units) between $K_{POM\text{-}500}$ and $K_{POM\text{-}55}$ that was significant for 10 out of 14 PAHs (t-test, 95%). As establishment of equilibrium in POM-500-water systems was previously tested [17,18] and both POM-500 and POM-55 consisted of the same type of POM (C-POM), this difference can only be attributed to a variation among different manufacturers. This means that for the use of POM in a routine-type fashion, either the supplier should be standardized or supplier-specific distribution ratios need to be established. The K-values measured at 8 °C (not shown) did not significantly deviate from the ones measured at 20 °C (t-test, 95%), so we used the values in Tables 2 and SI-1 for all the sampling times, regardless of exposure temperature. The absence of a temperature dependence is in agreement with earlier observations that K_{LDPE} varied by as little as 0.09 log-unit between 30 °C and 13 °C [19].

Porewater $C_{W,free}$ measured in the laboratory. PAH concentrations in POM-55 did not significantly increase from 10 d to 30 d of shaking (t-test, 95%; Table 3). Thus, in shaken sediment-water systems, equilibrium is established for POM-55 within 10 d. POM-500 is slightly underequilibrated after 30 d (Table 3), which is in contrast to earlier experiments where 28-30 d were shown to be enough for equilibration of this material [17,18]. At first glance a slight apparent underequilibration seemed to occur for the 2,3 and 4-ring PAHs in PDMS tubing (30 d; Table 3). There are two possible interpretations of this observation. One interpretation is that the complete equilibrium for the 5,6-ring PAHs is in contrast with the apparent underequilibration for the 2,3,4-ring ones, as one would expect longer equilibration times for larger PAHs with slower intrasampler diffusion and lower aqueous solubility. The apparent underequilibration of the 2,3,4-ring PAHs in PDMS tubing should then be attributed to analysis uncertainty. Alternatively, direct contact transfer and desorption from sediment within the unstirred passive sampler boundary layer may occur in shaken sediment slurries [19]. This would imply that the relation between hydrophobicity and uptake kinetics does not hold in sediment-water systems shaken in the laboratory.

Porewater $C_{W,free}$ of PYR and BAP was around 10 and 0.1 ng/L, respectively, at the outer harbor (NR) location; in the inner harbor locations these figures were 40-900 (PYR) and 3-20 (BAP) ng/L, respectively, the highest values occurring at the “hotspot” O10 sampling site (Table 4). For the other PAHs, trends were similar (Table 4 and Table SI-2). We found similar values for the different samplers (POM-55, POM-500 and PDMS tubing), giving credence to their reliability.

TOC-water distribution coefficients (K_{TOC}) were far above the values for amorphous organic carbon (AOC) obtained by a frequently used Linear Free-Energy Relationship (LFER; $\log K_{OC} = 0.98 \log K_{OW} + 0.38$ [25]; Figure 2). This is caused by the presence of carbonaceous geosorbents (CG; coal, kerogen, charcoal and soot) that sorb PAHs so strongly that overall TOC sorption can be increased by 2-3 orders of magnitude, as earlier observed for native pollutants in sediments [3,17,18,20,26,27] and soils [8]. For a sediment sample taken at a site approximately one km from the currently studied sites (Bjørvika, inner Oslo Harbor), the TOC consisted of 51% CG, of which almost half (46%) was carbonized [28]. BC contents of the current samples were significant (12-15% of TOC; Table 1) and even higher than for this previous inner Oslo Harbor sample (6.1% of TOC [27]).

Passive sampler field equilibration in overlying water. Temperatures in the field were 2-6 °C during equilibration (Table 1) and water currents were generally in the range of 2-4 cm/s (results not shown). At station NR (Outer Harbor) aqueous concentrations in overlying water were measured by both solvent extraction of water samples (total dissolved concentrations, $C_{W,total}$) and passive sampler exposure ($C_{W,free}$). Example curves for passive sampler equilibration in the field at Outer Harbor site NR are presented for PHE, PYR, BAP and BGP (Figure 2) as well as for NAP and CHR (Figure SI-1). There are four factors that need to be considered when assessing whether or not a passive sampler has reached equilibrium. First, there is the comparison of $C_{W,free}$ measured via passive samplers and $C_{W,total}$ measured by solvent extraction of water. Underequilibration causes $C_{W,free}$ to be lower than $C_{W,total}$. Second, sorption to POC and DOC in the water column has an effect on $C_{W,total}$. Because turbidity was negligible at site NR where the field time series experiment was performed (Table 1), we conclude that most of the aqueous OC was DOC. DOC contents were so low (2.4-2.8 mg/L; Table 1) that they only affected $C_{W,total}$ of the 5,6-ring PAHs. Thus, for these compounds a difference between $C_{W,free}$ (only dissolved) and $C_{W,total}$ (dissolved + DOC-bound) can also be caused by sorption to DOC. Third, differences between PAHs in apparent degree of equilibration can be used to deduce information on equilibrium: if equilibrium is reached for larger PAHs, it can also be expected for smaller PAHs with faster intrasampler diffusion and lower sampler-water distribution ratios. Fourth, increasing apparent $C_{W,free}$ in time indicates that equilibrium has not yet been established.

POM-55 and PDMS-SPME. In Table 5 are the ratios between $C_{W,free}$ and $C_{W,total}$, grouped for PAHs of similar size. It was observed that POM-55 and PDMS-SPME fibers reached equilibrium within

23-63 d for the 2,3,4-ring PAHs, as the ratios between $C_{W,free}$ (passive sampler extraction) and $C_{W,total}$ (direct solvent extraction) are all around one (Table 5) and constant over time (Table 5 and Figure 3). For the 5,6-ring PAHs, ratios between $C_{W,free}$ and $C_{W,total}$ were below one for all samplers. This difference can safely be attributed to PAH sorption to DOC and not to underequilibration, because i) the 28 µm PDMS-SPME fiber coatings and the 55-µm thin POM rendered the same apparent $C_{W,free}$, and ii) the ratios did not significantly (t-test; 95%) vary with field exposure time (Figure 3). This confirmed that it was realistic to assume that for the 5,6-ring PAHs sampler-water equilibrium was established within 23-63 d for POM-55 and SPME fibers.

PDMS tubing. The PDMS tubing closely approached equilibrium for all PAHs as i) the 2,3,4-ring PAHs reached $C_{W,free}$ / $C_{W,total}$ ratios around one after 23 d, ii) the apparent $C_{W,free}$ of 5,6-ring PAHs did not increase significantly between 23 and 97 d field exposure time (t-test, 95%). The observed slightly low ratios for this material might be caused by the uncertainty in its K-values (Table 2 and SI-1), since $C_{W,free}$ / $C_{W,total}$ ratios calculated with the K-values at the upper end of their 95%-confidence interval did not significantly differ from the ratios observed for equilibrated POM-55 and SPME fibers.

LDPE and POM-500. LDPE and POM-500 were in equilibrium after 119 d for the 2,3-ring PAHs, but clearly underequilibrated for the 5,6-ring PAHs and probably also the 4-ring ones (Figure 3; Table 5). The explanation that LDPE does not reach equilibrium for the largest PAHs is probably that its sorbs almost ten times more strongly than the other materials (Table 2), requiring the extraction of a correspondingly larger amount of water and the passage of the diffusion double layer of a larger amount of PAH for its equilibration. POM-500 is 5-500 times thicker than the other passive samplers and intrapolymer diffusion through the POM matrix is likely not rapid enough for the equilibration of this material under field conditions. This is in accordance with observations by Ahn et al. [29] who determined that PYR was still in the outer 500 µm of 2-mm POM pellets after 70 d in shaken systems [29], implying diffusion coefficients D in the order of 10^{-10}-10^{-11} cm^2/sec.

DOC-water partitioning. For station NR (Outer Harbor) DOC-water partitioning coefficients K_{DOC} could be calculated from the differences between $C_{W,total}$ and $C_{W,free}$ along with the DOC contents C_{DOC}

$$K_{DOC} = \frac{1}{C_{DOC}}\left(\frac{C_{W,total}}{C_{W,free}} - 1\right) \tag{1}$$

For $C_{W,total}$ average values of the five measurements were used. For $C_{W,free}$ average values determined with POM-55 and PDMS-SPME (all four time points) were used as equilibrium establishment was clearest for these materials. Log K_{DOC} was 5.7 ± 0.2 for BBF, 5.6 ± 0.3 for BKF, 5.9 ± 0.2 for BEP, 5.2 ± 0.3 for BAP, 6.1 ± 0.3 for IND and 5.9 ± 0.3 for BGP, respectively. For the other compounds $C_{W,free}$ and $C_{W,total}$ were not significantly different (t-test, 95%), ruling out the possibility to calculate K_{DOC}. The observed values of log K_{DOC} are 0.3-0.5 log-unit below LFER-calculated log K_{AOC}-values. This means that the aqueous DOC is somewhat less hydrophobic (factor of 2-3) than the average soil/sediment AOC, and much less hydrophobic (factor of 10-500) than the sediment TOC at the same site (Figure 2). This implies that the DOC at the currently studied field site probably contained very little BC. Such “dissolved/colloidal BC” has been observed in estuarine and coastal ocean DOC, at concentrations of 9 ± 6 % of total ultrafiltered DOC [30]. Our currently observed K_{DOC} values are in agreement with those reported by Krop et al. [31] who reviewed 900 literature K_{DOC} values for many different types of DOC and found K_{DOC} for PAHs with log $K_{OW} > 5$ to be 0.5-2 orders of magnitude below K_{OW} (and thus 0-1.5 orders of magnitude below K_{AOC}). The realistic values we obtained for K_{DOC} strengthen the conclusion that equilibrium was established in field-exposed POM-55, SPME fibers and, probably, PDMS tubing. This is to our knowledge the first time that K_{DOC} values are determined *in situ* without the need for isolation, filtration, centrifugation and/or transport of water samples to the laboratory.

Sediment-water flux direction. Estimates of flux directions were done via chemical activity (a) ratios that were directly calculated from $C_{W,free}$:

$$\frac{a_{porewater}}{a_{overlyingwater}} = \frac{C_{W,free}^{porewater}}{C_{W,free}^{overlyingwater}} \tag{2}$$

Activity ratios between porewater and overlying water ranged from 1.5 (5,6-ring PAHs in moderately contaminated NR sediment) to over 200 (2,3-ring PAHs in “hotspot” sediment O10; Table 6). This implies that there is disequilibrium between porewater and overlying water at all four stations and therefore there is a diffusive PAH flux from sediment to overlying water at all four stations. The diffusive flux is stronger at the hotspot O10 location (activity ratios 55-207) than at the moderately contaminated outer harbor location NR (activity ratios 1.5-16). Thus, there is a reasonable degree of mixing of the overlying water over a distance of approximately 1.5 km, and the sediment-water PAH flux increases with increasing PAH contents in the sediment porewater.

It is remarkable that the activity ratios so strongly decrease with PAH size at station NR (from 16 for the 2,3-ring PAHs to 1.5 for the 5,6-ring ones; Table 6). This can possibly be explained by biodegradation and/or relatively strong evaporation of the lighter PAHs in the water column.

The currently observed diffusive flux direction from sediment to water for PAHs is in accordance with Booij et al [19] who observed porewater-overlying water activity ratios of 1.2-44 for two Dutch harbor sediments. For PCBs, however, these authors observed a fair degree of equilibrium between porewater and overlying water.

Implications and recommendations. Measured values for $C_{W,free}$ in the sediment porewater varied by less than a factor of 2-3 for POM-55, POM-500 and PDMS tubing. This provides a valuable cross-validation in the absence of reference methods for the determination of $C_{W,free}$ (aim 1).

This study is the first one to report equilibrium passive sampling of water under relatively stagnant conditions (aim 2). If fast equilibration is desirable and low detection limits are required (e.g. for dioxins), POM-55 is probably the optimal passive sampler. If low detection limits are not required and measurements need to be fast, either SPME fibers or POM-55 can be used, with PDMS tubing as a good alternative. In the present study, all passive samplers were solvent-extracted before analysis. However, PDMS samplers also allow for thermal desorption in the GCMS injection chamber, which means that all analyte on the passive sampler actually passes the detector. This allows low detection limits even with small PDMS samplers such as PDMS coatings on glass or fibers.

Our passive sampler field data are time-integrated to a certain extent, depending on the equilibration time of the used passive sampler. The length of time over which measurements are time-integrated can probably be varied by adjusting the passive sampler thickness.

Chemical activity ratios between porewater and overlying water were over one at all locations and for all PAHs, and especially high at the inner harbor hotspot site O10 (aim 3). This indicates that the sediment is a PAH diffusion source, and that sediment remediation is potentially useful for PAH contamination in Oslo harbor, especially for the hotspot location. This is under the condition that no net PAH flux from air to water exists, such as shown for PCBs in the same outer Oslofjord water system [32].

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Table 1: Sampling site characteristics (location, sediment and water characteristics).

	NR (Outer Harbor)	**Q8 (Inner Harbor)**	**R6 (Inner Harbor)**	**O10 (Hotspot)**
Location				
Coordinates	N 59 53,625	N 59 54,3215	N 59 54,3746	N 59 54,2690
	E 10 45,075	E 10 45,4215	E 10 45,4779	E 10 45,3115
Water depth (m)	9.7	6.0	6.2	11.2
Sediment				
TOC (%)	3.0 ± 0.4	4.8 ± 0.1	4.8 ± 0.2	4.8 ± 0.1
BC (%)	0.25 ± 0.02	0.40 ± 0.08	0.31 ± 0.01	0.35 ± 0.05
BC:TOC (%)	12 ± 2	12 ± 3	15.7 ± 1.2	14 ± 2
PAH-14 (mg/kg) ^{1}	5.3 ± 0.6	14 ± 4	11 ± 3	82 ± 17
PCB-7 (µg/kg) ^{2,6}	n.m.	73	47	135
TBT (mg/kg)^{6}	n.m.	0.35	1.9	0.44
Oil (mg/kg)^{6}	n.m.	1300	1100	1700
Water				
Salinity (psu^{3})	36	37	35	37
T (°C)^{4}	2.1-9.8	6.2-19.1	5.4-20.5	5.6-19.7
TOC_{aq} (mg/L)^{4,5}	2.4-2.8	2.9-3.3	3.5-4.5	2.9-3.2
Turbidity (NTU)	0.0-0.1	0.1-0.4	3.8-4.3	n.m.

[1] sum of NAP = naphthalene, FLU = fluorene, PHE = phenanthrene, ANT = anthracene, FLUO = fluoranthene, PYR = pyrene, BAA = benz[a]anthracene, CHR = chrysene, BBF = benzo[b]fluoranthene, BKF = benzo[k]fluoranthene, BEP = benzo[e]pyrene, BAP = benzo[a]pyrene, IND = indeno[1,2,3-cd]pyrene, BGP = benzo[ghi]perylene (abbreviations used throughout the paper).

[2] sum of PCBs 28,52,101,118,153,138,180

[3] practical salinity units based on conductivity measurements.

[4] range for the five sampling time points.

[5] Total Organic Carbon in the unfiltered overlying water (probably all DOC, see text).

[6] determined by Analytica AS, Norway, using standard EPA procedures.

Table 2: Sampler-water distribution coefficients (log K; L/kg) for two example PAHs (PYR and BAP). For the other PAHs, log K-values are in Table SI-1.

	PYR	**PYR literature**	**BAP**	**BAP literature**
POM-55	4.04 ± 0.07[b]	Novel material	4.8 ± 0.2	Novel material
POM-500	3.67 ± 0.13	3.59[k], 3.76[l]	4.42 ± 0.13	4.46[k], 4.99[l]
LDPE	5.02 ± 0.03	4.88[h], 4.76[i], 5.0[j]	6.22 ± 0.12	5.72[h], 5.92[i], 6.3[j]
PDMS-SPME[a]	4.61 ± 0.16	3.80[c], 4.26[d], 4.44[e], 4.62[f], 4.86[g]	5.39 ± 0.16	4.86[e], 4.90[f], 5.39[g], 4.66[c]
PDMS tubing	4.41 ± 0.08	4.54[m]	4.90 ± 0.16	Not found

[a] PDMS coating on SPME fibers, [b] ± indicates standard deviation in triplicates, [c] ref. 15, [d] ref. 10 for FLUO, [e] ref. 11, [f] ref. 12, [g] ref. 14, [h] ref. 21, [i] ref. 19, [j] ref. 20, [k] ref. 18, [l] ref. 17, [m] ref. 16.

Table 3: Degree of equilibrium between passive samplers and NR sediment, expressed as ratio between apparent $C_{W,free}$ measured by the relevant passive sampler after 10 d or 30 d and $C_{W,free}$ measured by POM-55 after 30 d (where equilibrium was achieved), with standard deviations among the various PAHs in one group.

		2,3-ring	**4-ring**	**5,6-ring**
POM-55	10 d	0.8 ± 0.2	0.96 ± 0.05	1.0 ± 0.3
POM-500	30 d	0.47 ± 0.03	0.47 ± 0.01	0.62 ± 0.05
PDMS tube	10 d	0.32 ± 0.03	0.57 ± 0.02	0.63 ± 0.03
	30 d	0.60 ± 0.06	0.79 ± 0.03	1.16 ± 0.14

Table 4: Aqueous concentrations in porewater and overlying water at the four studied locations along with standard deviations in triplicates, for four example PAHs. For the other PAHs, C_W-values are in Table SI-2.

		PHE	**PYR**	**BAP**	**BGP**
Outer Harbor (NR)					
Porewater 0-5 cm[a]	$C_{W,free}$	18 ± 3	11.4 ± 0.8	0.12 ± 0.02	0.05 ± 0.02
Overlying water[b]	$C_{W,free}$	1.4 ± 0.8	2.3 ± 0.4	0.10 ± 0.05	0.02 ± 0.01
	$C_{W,\ total}$[c]	2.4 ± 0.6	2.2 ± 0.6	0.17 ± 0.05	0.10 ± 0.04
Inner harbor 1 (Q8)					
Porewater 0-5 cm[d]	$C_{W,free}$	15 ± 3	49 ± 2	4.1 ± 0.8	0.52 ± 0.12
Porewater 5-10 cm[d]	$C_{W,free}$	11 ± 2	58 ± 3	3.7 ± 0.8	0.49 ± 0.10
Overlying water[e]	$C_{W,free}$	0.9 ± 0.2	6.0 ± 2.6	0.24 ± 0.10	0.02 ± 0.01
Inner harbor 2 (R6)					
Porewater 0-5 cm[d]	$C_{W,free}$	12 ± 2	41 ± 14	2.89 ± 0.09	0.29 ± 0.04
Overlying water[e]	$C_{W,free}$	0.5 ± 0.1	3.6 ± 0.6	0.16 ± 0.03	0.02 ± 0.01
Inner harbor hotspot (O10)					
Porewater 0-5 cm[d]	$C_{W,free}$	92 ± 15	900 ± 100	21 ± 3	3.4 ± 0.7
Porewater 5-10 cm[d]	$C_{W,free}$	96 ± 17	560 ± 50	10.7 ± 1.6	1.34 ± 0.17
Overlying water[e]	$C_{W,free}$	0.44± 0.04	12.5 ± 1.2	0.52 ± 0.03	0.04 ± 0.01

[a] averages of determinations with POM-55 and PDMS tubing after 30 d shaking in the laboratory with summed standard deviations

[b] averages of determinations with POM-55, PDMS tubing and SPME equilibrated for > 30 d with summed standard deviations

[c] measured by total solvent extraction of water.

[d] determined with POM-500 equilibrated for 78 d in the laboratory

[e] determined with POM-55 equilibrated for 119 d in the field

Table 5: Ratio between apparent C_W measured with field-exposed passive samplers (freely dissolved) and directly in water (total dissolved), for NR (Outer Harbor site). Ratios under 1 indicate either underequilibrated passive samplers or binding to OC in the water.

Sampler	Eq. time (d)	2,3-ring	4-ring	5-ring	6-ring
POM-55	23	1.0 ± 0.5	0.6 ± 0.2	0.41 ± 0.09	0.20 ± 0.13
	63	1.4 ± 0.5	0.8 ± 0.3	0.58 ± 0.14	0.3 ± 0.3
	97	1.8 ± 1.0	1.0 ± 0.3	0.5 ± 0.3	0.14 ± 0.11
	119	1.0 ± 0.2	0.9 ± 0.3	0.40 ± 0.16	0.3 ± 0.3
POM-500	23	0.23 ± 0.03	0.3 ± 0.2	0.15 ± 0.06	0.05 ± 0.05
	63	0.48 ± 0.1	0.4 ± 0.3	0.13 ± 0.05	0.05 ± 0.06
	119	0.7 ± 0.4	0.5 ± 0.4	0.09 ± 0.02	0.01 ± 0.01
LDPE	23	0.7 ± 0.4	0.3 ± 0.3	0.04 ± 0.01	0.03 ± 0.02
	63	1.1 ± 0.3	0.5 ± 0.4	0.03 ± 0.01	0.010 ± 0.006
	97	0.8 ± 0.7	0.7 ± 0.6	0.02 ± 0.01	0.006 ± 0.003
	119	0.4 ± 0.2	0.8 ± 0.7	0.04 ± 0.02	0.009 ± 0.005
PDMS-SPME	23	1.0 ± 0.4	0.7 ± 0.3	0.50 ± 0.18	0.28 ± 0.12
	63	1.0 ± 0.1	1.0 ± 0.6	0.59 ± 0.18	0.37 ± 0.16
PDMS tubing	23	0.8 ± 0.3	0.6 ± 0.3	0.29 ± 0.14	0.12 ± 0.07
	63	1.0 ± 0.8	0.5 ± 0.4	0.19 ± 0.15	0.2 ± 0.2
	97	0.6 ± 0.3	1.0 ± 0.5	0.21 ± 0.13	0.18 ± 0.11
Average POM 55 + SPME[a]		1.2	0.8	0.5	0.3

[a] averages were taken for these materials (all four time points) as equilibrium establishment was clearest for these materials.

Table 6: Chemical activity ratios between porewater (0-5 cm layer) and overlying water, averaged for 2,3-ring, 4-ring and 5,6-ring PAHs.

	2,3 ring	4-ring	5,6-ring
Outer Harbor (NR)	16 ± 16[a]	3 ± 2	1.5 ± 0.9
Inner harbor 1 (Q8)	17 ± 7	9 ±1	18 ± 4
Inner harbor 2 (R6)	22 ± 5	13 ± 4	16 ± 2
Inner harbor hotspot (O10)	207 ± 53	128 ± 61	55 ± 29

[a] standard deviations are summations of standard deviations in $C_{W,free}$ in porewater and in overlying water, respectively.

Figure 1: Example sorption isotherms for four PAHs sorbed to PDMS tubing. Linear sorption was observed with slopes 0.82 ± 0.04, 0.96 ± 0.07, 1.01 ± 0.03, and 1.11 ± 0.09 for PHE, PYR, BAP, and BGP, respectively.

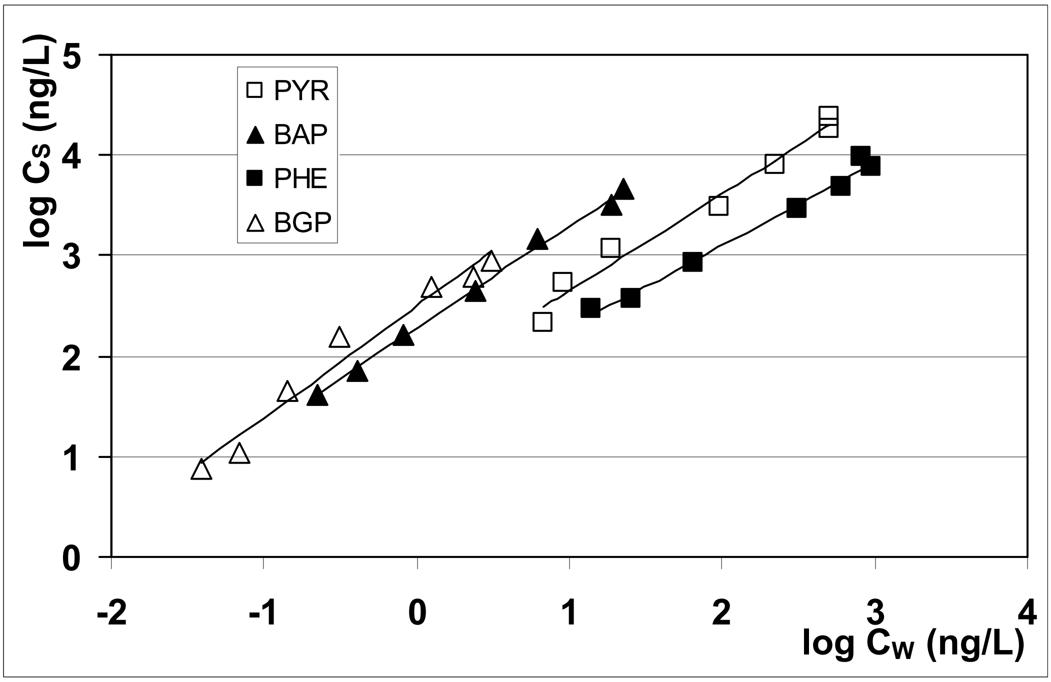


Figure 2: Log K_{TOC} vs. Log K_{OW} for the four studied sediments from Oslo Harbor. Standard deviations averaged 0.07 log-units (range 0.02-0.21). It was observed that K_{TOC} is 1-3 orders of magnitude above K_{AOC} for amorphous organic carbon.

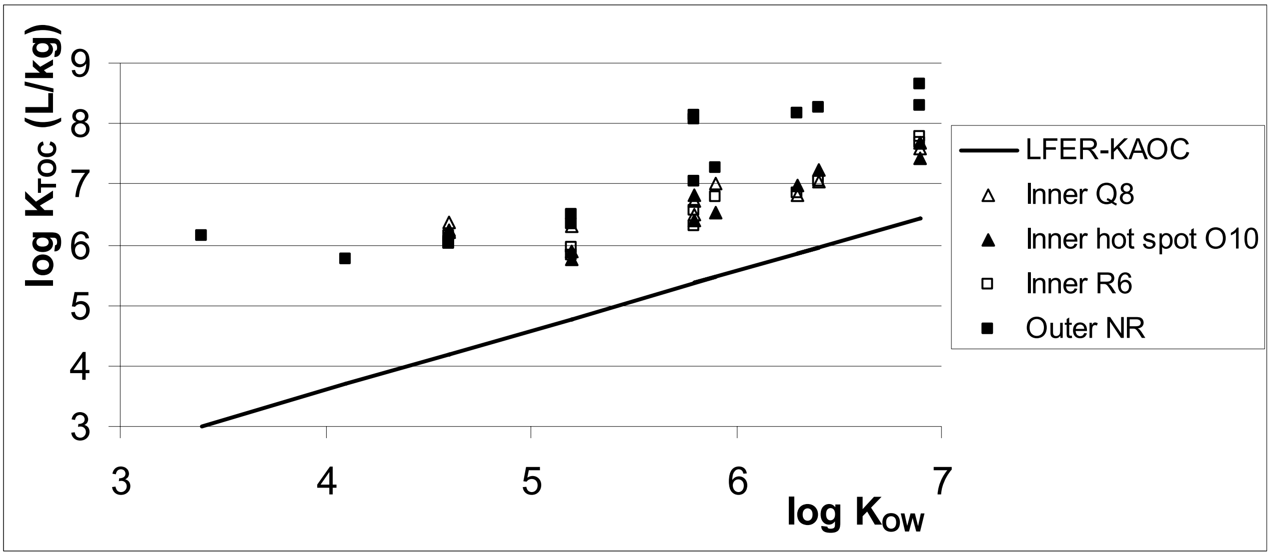
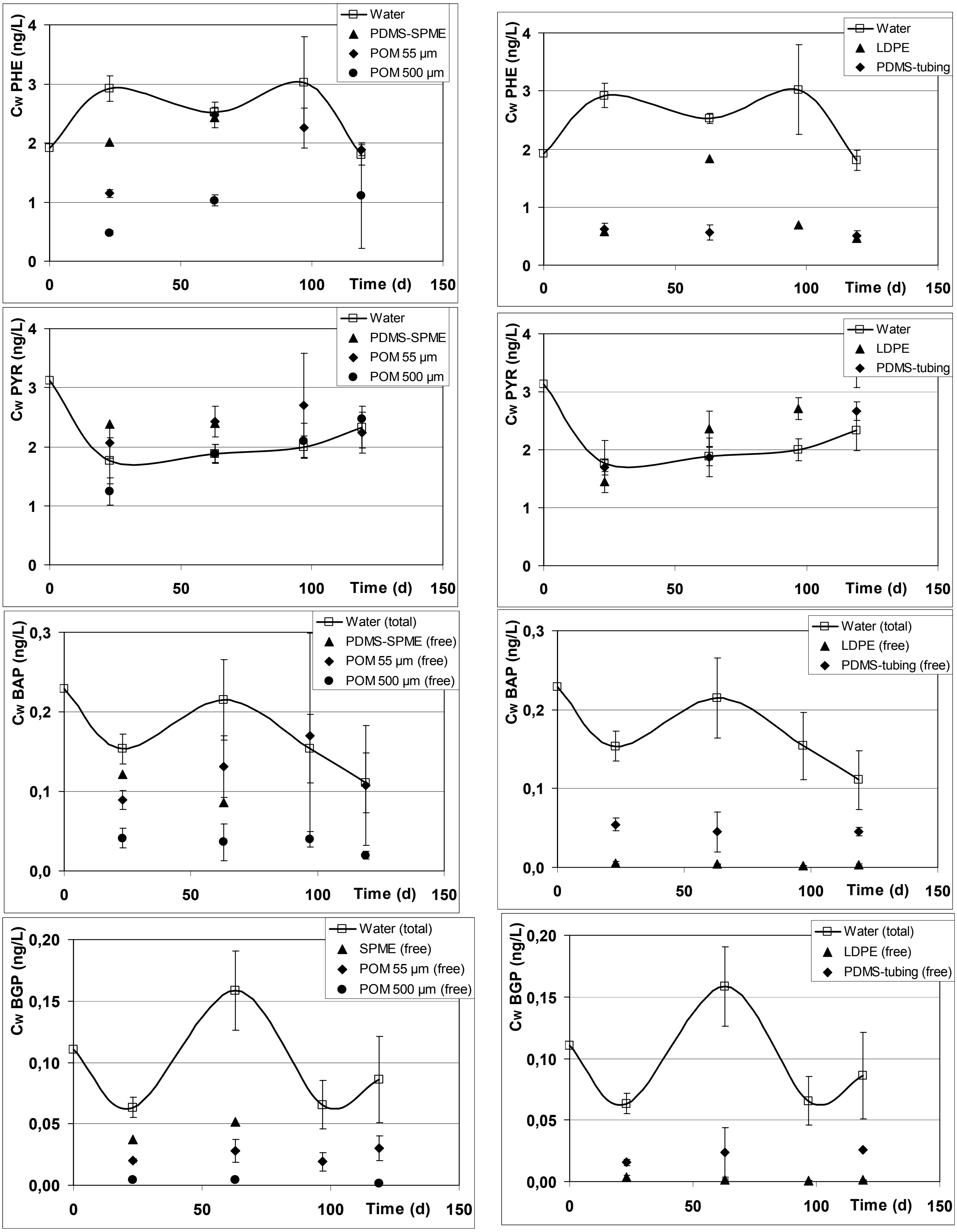


Figure 3: Field exposure of the passive sampler materials at station NR (outer harbor). Plotted are the apparent $C_{W,free}$-values calculated with the K-values from Table 2, as well as the total water concentrations $C_{W,total}$ measured by solvent extraction (open squares joined by solid lines). Example curves are given for PHE, PYR, BAP and BGP. For NAP and CHR, similar figures are presented in the SI. Error bas denote standard deviations in triplicate measurements. The absence of an error bar indicates that only duplicate samples were analyzed.



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