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Field comparison of passive sampling and biological approaches for measuring exposure to PAH and alkylphenols from offshore produced water discharges

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ABSTRACT

Polycyclic aromatic hydrocarbons (PAH) and alkylphenols (AP) that are present in routine discharges of produced water (PW) from the offshore industry continue to cause concern. The suitability of biological methods and chemical based passive samplers to determine exposure to these compounds was tested by deploying them around an oil installation and at reference locations in the North Sea. PAH and AP were analysed either as parent compounds in passive samplers and mussel tissue or as metabolites in fish bile. Generally the pattern of exposure relative to proximity to the discharge was represented by mussels, SPMDs and fish for PAH. Fish and SPMDs showed good correlation for PAH accumulations, whereas some differences were apparent between mussels and SPMDs. POCIS was the only technique tested that could accurately measure the most abundant AP in PW. The advantages of biologically independent measures of exposure for inclusion in discharge monitoring studies are outlined.

1. Introduction

The offshore oil and gas industry contributes a significant input of organic pollutants to the marine environment through routine operational discharges. By far the most significant discharge is that of produced water (PW) which is largely a mixture of water injected to aid oil extraction and formation water which is naturally occurring within the reservoir. In the North Sea and Norwegian Sea the quantity of PW is increasing in line with the age of the wells and reached 119×10^6 m^3 in 2008 (OLF, 2009). In the light of this increase, as well as the increasing pressure for further exploration in areas assumed particularly sensitive to contamination such as the Arctic, the need for effective and appropriate monitoring is growing. In addition, there is political ambition within Norway of discharges with "zero effect" to the environment (SFT, 2004). The composition of PW is both complex and highly variable (Neff, 2002; Utvik, 1999). Of the organic constituents, polycyclic aromatic hydrocarbons (PAH) and alkylphenols (AP) are often regarded to contribute significantly to the environmental risk (Johnsen et al., 1994). Whilst the bulk of oil present in PW is removed before discharge (the current limit is 30 mg oil L^{-1}), significant quantities of these compounds are still released due to the large volumes involved, roughly 336 tonnes of AP and 81 tonnes of PAH in the Norwegian sector in 2008 (OLF, 2009).

Assessment of the overall impact of such inputs of chemicals is complex due to rapid dilution in the receiving waters and a lack of studies considering ecologically relevant endpoints (Hylland, 2006; Hylland et al., 2006b). Thus, sensitive monitoring techniques are required in order to assess the potential for biological effects *in situ*. In the Norwegian sector the offshore operators collectively carry out a 'water column monitoring survey' (WCMS) most years. The objective of the survey is to assess the extent to which discharges from an oil production platform affect organisms in the water column. The WCMS currently involves the caging of blue mussels (*Mytilus edulis*) and Atlantic cod (*Gadus morhua*) at strategic points around a chosen discharge point and at reference locations. Chemical exposure is measured as body burden in mussels or as metabolites in fish bile. Additionally a suite of sensitive biomarkers are used to assess the health of these organisms (Brooks et al., in press; Hylland et al., 2006a, 2008).

Another technique that has been shown to be useful for assessing exposure to organic compounds in PW is the use of passive sampling devices (PSDs) (Durell et al., 2006; Harman et al., 2010, 2009b; Utvik et al., 1999; Utvik and Johnsen, 1999). Such devices accumulate contaminants by diffusive and partitioning processes, sampling is unattended and extraction occurs simultaneously. PSD techniques may often be preferable to discrete sampling methods offering large volume sampling and low detection limits (Lebo et al., 1995). They may also compensate for fluctuating discharges by measuring time integrated concentrations (Gale, 1998; Gourlay-France et al., 2008; Hawker, 2010). The semipermeable membrane device (SPMD) (Huckins et al., 1990a,b) remains

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the most widely used PSD for measuring hydrophobic organic chemicals in water. Of the studies available that use SPMDs, consideration of PAH dominates (Esteve-Turrillas et al., 2007). However, SPMDs are not suited to sampling compounds with log K_{ow} < 3.0 (Huckins et al., 2006) including the AP most prevalent in PW (Harman et al., 2008a). Instead the polar organic chemical integrative sampler (POCIS) may be applied (Alvarez et al., 2004). This sampler has been shown to successfully accumulate a wide range of polar compounds such as pharmaceuticals, personal care products, polar pesticides and AP (Alvarez et al., 2005; Arditsoglou and Voutsa, 2008; Harman et al., 2009b; MacLeod et al., 2007; Mazzella et al., 2007; Togola and Budzinski, 2007). Thus, simultaneous deployment of SPMDs and POCIS allows measurement of contaminants with a broad range of physicochemical properties.

Due to similarities in uptake processes of chemicals, deployments of passive samplers are often used to infer exposure to biota. PSDs may have a number of advantages over the use of biomonitoring organisms (Table 1) and numerous studies of side by side comparisons have been reported. For SPMDs, deployments alongside bivalves, especially mussels, dominate (Huckins et al., 2006) and a model describing the concentration ratios has been proposed (Booij et al., 2006). Several studies also compare uptake of contaminants by SPMDs to fish and strong correlations have been shown for compounds that are poorly metabolised (Meadows et al., 1998; Wang et al., 2002). As PAH are readily metabolised by fish a few studies have attempted to correlate metabolites in fish bile directly with accumulations in SPMDs with reasonable relationships presented (Harman et al., 2009a; Verweij et al., 2004). Thus, when the most significant exposure pathway is through the dissolved phase, then good correlations between SPMD PAH accumulations and PAH metabolites in fish bile can be expected (Harman et al., 2009a). This is due to the similarity in uptake across fish gills and the low density polyethylene membrane used in SPMDs (Huckins et al., 2006).

The overall objective of this work was to compare currently used biological methods to passive sampling devices for measuring *in situ* exposure to PAH and AP from offshore PW discharges.

2. Methods

2.1. Chemicals and equipment

SPMDs (91.4 × 2.5 cm LDPE tubing, containing 1 mL triolein), were spiked with five deuterated PAH (acenaphthene-d10, fluorene-d10, phenanthrene-d10, chrysene-d12 and benzo[e]pyrene-d12) as performance reference compounds (PRCs) for exposure adjustment (Booij et al., 1998; Huckins et al., 2002). POCIS contained Oasis® HLB sorbent between two discs of polyethersulphone membrane (0.1 μm pore size) with a surface area of 42 cm^2 and sorbent mass of 240 mg. Both passive sampling devices were obtained from ExposMeter (Tavelsjo, Sweden). Solvents were from Rathburn (Walkerburn, Scotland) except for cyclohexane (J.T. Baker, Deventer, Holland) and were of HPLC grade or better. All glassware was baked in a muffle furnace at 560 °C before use.

2.2. Deployment

Organisms and PSDs were deployed during the WCMS in 2008 and 2009. The purpose of the survey was to monitor bioaccumulation and biomarker responses in mussels and fish in the vicinity of the Ekofisk oil production platform (Sundt et al., 2008). The choice

Table 1
Advantages and disadvantages of using the different techniques discussed for measuring PW originating AP and PAH.

	Mussels	SPMDs	Fish	Pocis
Suitability for measuring PW AP/PAH	Very good (PAH) not accumulated (AP)	Very good (PAH) poor for most relevant AP	Good (PAH) limited (AP)	Very good (AP) not accumulated (PAH)
Number of compounds detected	<29 PAH	29 PAH	9 OH–PAH, 5 OH–AP	>60 AP
Pattern of exposure represented	Yes PAH	Yes PAH	Limited	Yes AP
Ability to measure exposure to other PW relevant compounds?	Likely for hydrophobic compounds present in significant quantity, e.g. decalins	More or less any compound with log k_{ow} > 3.0, e.g. hopanes, carbazoles, decalins	Complicated method development required	More or less any compound with log k_{ow} > 3.0, e.g. organic acids. Configuration easily modified
Initial concentrations of contaminants	Some PAH signal always present	Very low (ng) for most PAH[a]	Some PAH/AP signal always present	Very low (pg) for AP
Ease of deployment	Moderate	Easy	Difficult	Easy
Correction for spatial and temporal differences in deployment conditions?	No	Yes where an appropriate PRC approach is used	No	May be inferred from SPMD PRC results
Typical variation	Moderate (average RSD 10–41%)	Low (average RSD 9–17%)	Very high (average PAH RSD 24–104%, AP 44–182%)	Low-moderate (average RSD 7–32%)
Sensitivity, as accumulations/LOQ[b]	Good (33.7 for PAH)	Generally very good (15.6 for PAH)[c]	Poor (1.3 for AP, 2.5 for PAH)	Good (14.3, for AP)
Estimation of exposure water concentrations?	Possible for PAH using literature BAFs, but large uncertainties	Excellent, using the PRC approach	Not possible, some evidence that rates of metabolism are not independent of concentrations	Not as accurate as for SPMDs, but not hampered by any biological processes
Understanding of uptake process	Complicated, partly dependent on environmental variables	More easily quantifiable then for organisms	Complicated, partly dependent on environmental variables	More easily quantifiable then for organisms
Results in extreme conditions?	No	Yes	No	Yes
Overall ecological relevance of results	A well accepted measure of bioaccumulation. Mussels not naturally present	Exposure to biota may be inferred	Highly relevant species	Low, concentrations must be compared to laboratory studies
Direct measurement of biological effects	Yes	No, extracts may be used in bioassay testing	Yes	No, extracts may be used in bioassay testing

[a] Alkylated naphthalenes are an exception.
[b] Average accumulations for exposure stations 3 and 4. Only compounds measured in both matrices considered. LOQ determined as average blank value + 10 × SD.
[c] C3-alkylated naphthalenes not included due to exception blank value.