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Oil well produced water discharges to the North Sea. Part I: Comparison of deployed mussels (*Mytilus edulis*), semi-permeable membrane devices, and the DREAM model predictions to estimate the dispersion of polycyclic aromatic hydrocarbons

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Abstract

The oil companies operating in the Norwegian sector of the North Sea have conducted field studies since the mid-1990s to monitor produced water discharges to the ocean. These studies have been used to refine monitoring methods, and to develop and validate a dispersion and impact assessment model. This paper summarizes monitoring data from surveys conducted in two major oil and gas production areas, and compares the results to concentrations of polycyclic aromatic hydrocarbons (PAH) in surface waters predicted by the dose-related risk and effect assessment model (DREAM). Blue mussels and semi-permeable membrane devices (SPMDs) were deployed in the Ekofisk and Tampen Regions and analyzed for more than 50 PAH. PAH concentrations in ambient seawater were estimated based on the mussels and SPMD concentrations, and compared to model predictions. Surface water total PAH concentrations ranged from 25 to 350 ng/L within 1 km of the platform discharges and reached background levels of 4–8 ng/L within 5–10 km of the discharge; a 100,000-fold dilution of the PAH in the discharge water. The PAH concentrations in surface water,

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predicted by three methods, compared well for the Ekofisk Region. The model predicted higher concentrations than the field-based methods for parts of the Tampen Region; particularly the most tidally influenced areas. Tidally-mediated fluctuations in PAH concentrations in surface water must be considered because they affect the estimation of PAH concentrations from mussel and SPMD residue data, and the predictions by the DREAM model. Predictions using mussels, SPMDs, and modeling support and complement each other; all are valuable tools for estimating the fate and impact of chemical contaminants in produced water that are discharged to the ocean.

Keywords: SPMDs; Mussels; North Sea; Offshore platforms; Monitoring; Petroleum hydrocarbons

1. Introduction

The discharge of produced water from offshore oil and gas production has received increased attention in recent years, due to the potential ecological risks posed by some of the chemicals in the produced water. Produced water is fossil water that has been trapped with oil and gas in the geologic reservoir deep below the earth for millions of years (Neff, 2002). It is produced from a well together with the fossil fuels. On many offshore platforms throughout the world, the produced gas, oil, and water are separated and the produced water is treated to remove dispersed oil and discharged to the ocean.

Produced water usually is the largest volume waste from offshore oil and gas production facilities; discharge of produced water to the North Sea reached an annual volume of close to 400 million m^3/year in 2003; roughly 100 million m^3 of produced water was discharged in the Norwegian sector in 2000 (Røe, 1998). About 30% of the produced water discharged to the entire North Sea is from oil and gas production fields in the Norwegian sector.

Regulations limit the concentration of total petroleum hydrocarbons to 40 mg/L in produced water discharged in the Norwegian sector of the North Sea. However, it is widely recognized that total petroleum hydrocarbons may not adequately represent the potential environmental impact of produced water and other oil and gas production discharges (Carroll et al., 2000; Johnsen et al., 2000). The hydrocarbon component of the discharge is comprised of chemicals with varying potential to cause environmental harm; non-hydrocarbon constituents of produced water also may be important contributors to ecological risk. In addition, the chemical composition of produced water from different sources varies widely (Neff, 2002; Røe, 1998; Røe Utvik, 1999).

Recognizing the complexity of assessing and managing the potential ecological effects of produced water discharges, and the limitations of the current approach, the Norwegian oil industry introduced the environmental impact factor (EIF) as a tool for estimating potential risk to marine organisms from produced water discharges and developed a strategy to reach zero *harmful* discharge by the year 2005 (Johnsen et al., 2000; SFT, 1999). In 1999, the Norwegian state pollution control agency (SFT) launched a comprehensive environmental monitoring program focusing on predicting the potential effects caused by produced water discharges to the water column, requiring the oil industry to monitor contaminants in and potential effects to water column organisms. The work described in this paper is based on the results of studies in support of the long-term programs of SFT and the industry.

Produced water has a complex chemical composition that includes dispersed oil, dissolved hydrocarbons, organic acids, alkylated phenols, metals, and traces of production chemicals added to the oil or produced water during production and treatment (Neff, 2002). The composition of produced water varies from one well to another and a number of studies have been performed to characterize the produced water from fields in the North Sea (Røe Utvik, 1999). In this study, we have focused on PAH, and related cyclic and heterocyclic compounds, because these chemicals are considered to be the major contributors to any ecological effects of produced water and are given particular attention in the management of discharges in Norway (Neff, 2002; Røe, 1998; SFT, 1999).

Several studies have been performed to monitor and model the fate and effects of produced water discharges to the Norwegian sector of the North Sea (Durell et al., 2000, 2004; Johnsen et al., 1998; Neff et al., 2006; Røe Utvik et al., 1999; Røe Utvik and Johnsen, 1999). These studies were designed partly to serve as baseline studies for future monitoring programs, and partly to evaluate, optimize, and implement different sampling, monitoring, and assessment techniques. Because of the rapid dilution of discharged produced water in the North Sea, sampling methods must be able to detect ultra-trace concentrations of the chemicals of concern in the water column. Sampling techniques that rely on deployment of bivalves and SPMDs, which concentrate and integrate contaminants over time, are particularly useful for sampling the organic compounds of interest from produced water in ambient surface waters (Røe Utvik et al., 1999). Bivalves and SPMDs have been shown to be effective for measuring bioaccumulative organic contaminants, which are of particular interest in the Norwegian produced water management initiatives.

The study described in this paper is based on the use of field-deployed blue mussels (*Mytilus edulis*) and SPMDs to collect time-integrated hydrocarbon data, and to estimate concentrations of PAH from produced water in the water column. The PAH concentrations in seawater, estimated from mussels and SPMDs, also are compared to results from dispersion modeling using the DREAM model. DREAM is based on field-specific discharge volumes, discharge composition data, and field hydrological data. Dispersion modeling also is an important component of the Norwegian produced water management program. The primary objectives of this paper are to present estimates of concentrations of produced water originating PAH in the ocean, the fate of the PAH, and compare field-based and modeled results. The paper is not intended to in detail describe the sampling techniques used to generate the field-based data, or discuss the merits and drawbacks of those methods (such information has been presented in other papers by these and other authors). The data from two field studies are described in this paper: a survey in the Tampen Region in 1997 (Johnsen et al., 1998; Røe Utvik et al., 1999) and one in the Ekofisk Region in 1999 (Durell et al., 2000). A companion paper (Neff et al., 2006) compares the ecological risk predicted based on these field measurements to risk predicted using DREAM.

2. Methods

Table 1 lists the major oil and gas production platforms in the Tampen and Ekofisk Regions (Fig. 1), recent produced water discharge volumes, discharge depths, and the approximate concentrations of oil and the three major aromatic classes of PAH compounds discussed in this study. These compound classifications are based on the Norwegian environmental regulations. Note that naphthalene and its alkyl homologues are listed separately from other 2–3-ring PAH.

Table 1
Approximate discharge volumes and concentrations of key compound classes for produced water in the Tampen and Ekofisk Regions

Platform	Discharge		Concentration (mg/L)[a]			
	Volume (m^3/day)[a]	Depth (m)	Dispersed oil	Naphthalenes	PAH 2/3-Ring	PAH 4/5-ring
Tampen Region						
Statfjord A	28,200	40	23.3	1.29	0.149	0.003
Statfjord B	21,400	40	28.3	1.26	0.216	0.004
Statfjord C	24,500	40	22.4	0.90	0.086	0.001
Gullfaks A	15,700	18	26.3	0.85	0.071	0.001
Gullfaks B	24,800	20	22.9	1.20	0.129	0.002
Gullfaks C	19,400	28	32.3	0.99	0.097	0.001
Veslefrikk	7400	6	31.8	1.40	0.129	0.002
Troll A	2	20	15.9	0.48	0.009	0.000
Troll B	19,100	20	25.3	1.43	0.118	0.005
Snorre TLP	12,100	15	27	1.59	0.390	0.005
Oseberg C	2550	15	35	1.42	0.197	0.006
Oseberg FS	4800	19	35	1.11	0.111	0.003
Brage	3230	1	36.5	1.16	0.139	0.006
Total	183,000					
Ekofisk Region						
Ekofisk K	3300	22	9.7	0.47	0.046	0.0005
Ekofisk J	1990	39	64[b]	1.05	0.066	0.0007
Eldfisk B	255	12	31.8	0.58	0.042	0.0005
Eldfisk A	167	13	41.4	0.87	0.091	0.0010
Tor E	1520	2	14.7	0.25	0.012	0.0002
Valhall	255	2	21	0.23	0.010	0.0001
Ula	1270	2	26	3.59	0.230	0.0052
Gyda	2900	2	19	0.50	0.040	0.0006
Total	11,700					

PAH, polycyclic aromatic hydrocarbon.
[a] The discharge volume and oil concentrations represent the field survey years (1997 and 1999 for Tampen and Ekofisk, respectively). The PAH compound concentrations are from 2002 because they were deemed more reliable and representative.
[b] The oil/water separation system was malfunctioning when Ekofisk 2/4J was sampled; this is likely a non-representative elevated value.

2.1. Field work

The data presented in this paper were generated from two field surveys. The first survey was conducted in 1997 in the Tampen Region using the supply vessel *M/S Ocean Knarr*, and the second was in 1999 in the Ekofisk Region using the vessel *Far Spirit*. The Tampen study area was in the western part of what SFT defines as the Statfjord and Oseberg Regions, and the Ekofisk study area was in the southwestern section of the Ekofisk Region (Fig. 1). Produced water discharge data and contaminant dispersion modeling were used to select a total of 10 sampling stations for the Tampen survey and 15 stations for the Ekofisk survey (Fig. 2). Sampling stations were located near and along transects away from major discharges to measure contamination near-field (within ~1 km), at intermediate locations to assess general regional impact (within ~10 km), and distant from know releases (>50 km) at locations expected to represent background levels.

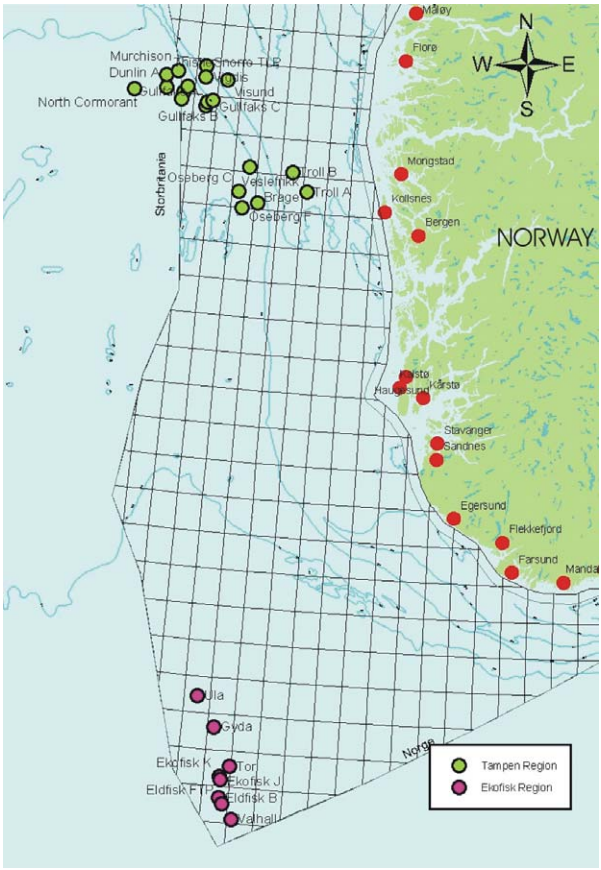

Fig. 1. Major oil and gas production installations in the study regions.

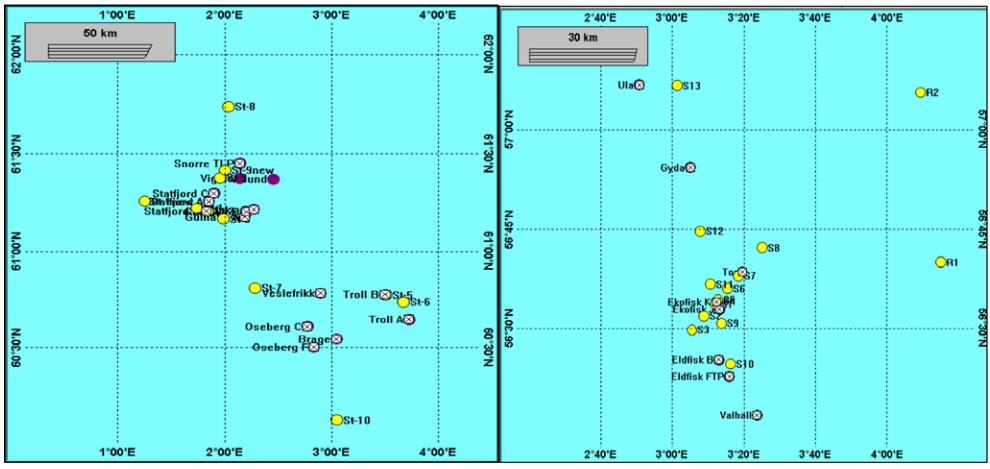

Fig. 2. Sampling locations (yellow station markers) and platforms in the Tampen and Ekofisk Regions.

A variety of field samples, including bulk water grab samples, field-processed solid-phase extracted water samples, in situ large-volume water samples, plankton, mussel, and SPMD samples, were collected for evaluation purposes and to meet different data objectives (Durell et al., 2000; Johnsen et al., 1998; Røe Utvik et al., 1999; Røe Utvik and Johnsen, 1999). The rapid dilution of the produced water following discharged to the North Sea results in near-background levels within a short distance of the discharge, and ultra-sensitive sampling techniques are required to detect the contaminants. Limited success was achieved with direct water sampling techniques (i.e., direct grab sampling, solid-phase extraction sampling, and in situ large-volume sampling). Sampling techniques that relied on the deployment of mussels and SPMDs, which concentrate bioaccumulative contaminants over an extended period of time, were more useful for most purposes (Røe Utvik et al., 1999).

This paper presents results based on deployed mussels and SPMDs, both of which have been shown to effectively concentrate bioavailable hydrophobic organic contaminants in the water column (Axelman et al., 1999; Baussant et al., 2001; Huckins et al., 1990; Lebo et al., 1992, 1996; Peven et al., 1996; Prest et al., 1992; Richardson et al., 2003; Salazar and Salazar, 1995), and can be used to estimate low concentrations of dissolved and finely dispersed organic contaminants in the water column (Gustafson and Dickhut, 1997; Huckins et al., 1993, 1999; Luellen and Shea, 2002; Neff and Burns, 1996). Mussels and SPMDs equilibrate with, or continuously sample, contaminants in the ambient water; hydrocarbon residues in them are generally proportional to the integrated time-averaged concentrations of bioavailable contaminants in the water column. In contrast, a water sample collected at a fixed time and location may not be representative of the typical contamination at a location. SPMDs and mussels also are particularly effective in selectively capturing the bioaccumulative organic compounds that are of particular interest for environmental management.

Blue mussels (*M. edulis*) were obtained from a mussel farm in a Norwegian fjord. Approximately 100 mussels of 4–6 cm length were deployed per station. The SPMDs were purchased from the licensed manufacturer (EST, St. Joseph, MO, USA) and were of a standard size (91-cm long × 2.54-cm wide, filled with 1 mL Triolein). The mussels and SPMDs were placed in stainless steel cages, attached to a rig wire, and secured at a depth of 10 m at each station. They were deployed in early May and were retrieved 28 days later, with no evidence of mussel spawning. The survival exceeded 90% for the retrieved mussels. The SPMDs and mussels were placed in pre-cleaned glass containers and frozen until laboratory analysis.

2.2. Sample analysis

Whole soft tissues of mussels and SPMDs were extracted and analyzed at Battelle (Duxbury, MA) for 53 organic compounds (Table 2) of the types found in produced water (e.g., parent and alkylated PAH, heterocyclic thiophenes, and decalins). Approximately half of these compounds are of particular interest for North Sea environmental management. These are the 16 US EPA priority pollutant PAH, dibenzothiophene, and the C1- through C3-alkylated homologues of naphthalene, phenanthrene, anthracene, and dibenzothiophene; a total of 26 chemicals or chemical groups. These 26 analytes are identified in Tables 2 and 3, along with the compound groups to which they belong for the purposes of contaminant modeling (described below) and environmental impact management.

Table 2
Estimated water concentrations (ng/L) based on mussel (*Mytilus edulis*) data

	Modeling group	Estimated constants		Example tissue data Tampen S-1 (ng/g)[a]	Tampen stations			Ekofisk stations		
		log K_{ow}	$10^{-[A\log(K_{ow})+B]}$		S-1 (ng/L)	S-5 (ng/L)	S-10 (ng/L)	S-4 (ng/L)	S-6 (ng/L)	R2 (ng/L)
Decalin		4.2	0.0022233	0.47	0.45	8.06	0.00	5.50	0.28	0.05
C1-decalins		4.6	0.0009141	3.00	1.17	13.9	0.00	14.1	1.86	0.00
C2-decalins		5.0	0.0003758	12.6	2.02	13.7	0.00	14.8	3.40	0.00
C3-decalins		5.4	0.0001545	22.0	1.45	7.78	0.00	5.30	1.86	0.00
C4-decalins		5.8	0.0000635	31.3	0.85	3.38	0.00	2.41	1.05	0.00
Benzo[b]thiophene		3.12	0.0245019	nd	0.00	0.00	0.00	0.00	0.00	0.00
C1-benzothiophenes		3.71	0.0066047	nd	0.00	0.00	0.00	0.00	0.00	0.00
C2-benzothiophenes		4.1	0.0027765	nd	0.00	0.00	0.00	0.00	0.00	0.00
C3-benzothiophenes		4.5	0.0011416	nd	0.00	0.00	0.00	0.00	0.00	0.00
C4-benzothiophenes		5.0	0.0003758	nd	0.00	0.00	0.00	0.00	0.00	0.00
Naphthalene	Naphthalenes	3.37	0.0140589	1.30	7.85	10.6	4.83	4.51	4.28	3.61
C1-naphthalenes	Naphthalenes	3.87	0.0046286	1.58	3.14	6.92	1.45	3.67	1.77	0.46
C2-naphthalenes	Naphthalenes	4.37	0.0015239	2.68	1.75	10.1	0.61	8.21	2.81	0.18
C3-naphthalenes	Naphthalenes	4.90	0.0004695	3.63	0.73	7.36	0.11	6.13	1.73	0.22
C4-naphthalenes		5.30	0.0001930	5.37	0.44	3.26	0.00	2.05	0.55	0.05
Biphenyl		3.90	0.0043301	0.21	0.40	1.03	0.24	0.83	0.58	0.12
Acenaphthylene	2/3-Ring	4.00	0.0034674	nd	0.00	0.00	0.00	0.00	0.00	0.00
Acenaphthene	2/3-Ring	3.92	0.0041419	nd	0.00	0.00	0.00	0.00	0.00	0.03
Dibenzofuran		4.12	0.0026558	0.18	0.20	0.30	0.09	0.30	0.28	0.23
Fluorene	2/3-Ring	4.18	0.0023243	0.50	0.49	1.10	0.16	0.93	0.46	0.18
C1-fluorenes		4.97	0.0004017	1.66	0.29	1.37	0.04	1.17	0.31	0.04
C2-fluorenes		5.20	0.0002410	12.6	1.31	2.91	0.00	1.80	0.55	0.06
C3-fluorenes		5.70	0.0000793	33.4	1.13	1.55	0.00	0.48	0.12	0.00
Anthracene	2/3-Ring	4.54	0.0010445	nd	0.00	0.00	0.00	0.24	0.07	0.00
Phenanthrene	2/3-Ring	4.46	0.0012477	1.50	0.80	2.94	0.29	3.05	0.78	0.19
C1-phenanthrenes/anthracenes	2/3-Ring	5.14	0.0002754	5.44	0.64	2.73	0.09	3.41	0.67	0.22
C2-phenanthrenes/anthracenes	2/3-Ring	5.46	0.0001352	16.1	0.93	2.88	0.00	2.76	0.50	0.06
C3-phenanthrenes/anthracenes	2/3-Ring	5.92	0.0000487	56.8	1.18	1.70	0.00	0.89	0.12	0.03
C4-phenanthrenes/anthracenes		6.32	0.0000200	14.1	0.12	0.28	0.00	0.13	0.02	0.00

Dibenzothiophene	2/3-Ring	4.38	0.0014904	0.39	0.25	0.38	0.04	0.45	0.19	0.04
C1-dibenzothiophenes	2/3-Ring	4.86	0.0005130	3.37	0.74	1.22	0.00	1.12	0.38	0.07
C2-dibenzothiophenes	2/3-Ring	5.50	0.0001237	12.6	0.67	1.00	0.00	0.63	0.18	0.02
C3-dibenzothiophenes	2/3-Ring	5.73	0.0000742	8.96	0.28	0.40	0.00	0.35	0.09	0.01
C4-dibenzothiophenes		6.1	0.0000326	6.83	0.10	0.12	0.00	0.07	0.01	0.00
Fluoranthene	4/5-ring	5.22	0.0002305	0.55	0.05	0.20	0.00	0.08	0.05	0.07
Pyrene	4/5-ring	5.18	0.0002519	2.26	0.24	0.19	0.00	0.18	0.04	0.01
C1-fluoranthenes/pyrenes		5.5	0.0001237	1.87	0.10	0.58	0.00	0.28	0.04	0.02
C2-fluoranthenes/pyrenes		5.80	0.0000635	4.04	0.11	0.40	0.00	0.24	0.02	0.00
C3-fluoranthenes/pyrenes		6.28	0.0000219	2.49	0.02	0.09	0.00	0.07	0.00	0.00
Benz(a)anthracene	4/5-ring	5.91	0.0000498	0.32	0.01	0.01	0.00	0.00	0.00	0.00
Chrysene	4/5-ring	5.61	0.0000969	1.45	0.06	0.13	0.00	0.18	0.02	0.02
C1-chrysenes		6.14	0.0000299	1.60	0.02	0.06	0.00	0.09	0.01	0.00
C2-chrysenes		6.43	0.0000157	nd	0.00	0.02	0.00	0.06	0.00	0.00
C3-chrysenes		6.94	0.0000051	nd	0.00	0.00	0.00	0.00	0.00	0.00
C4-chrysenes		7.36	0.0000020	nd	0.00	0.00	0.00	0.00	0.00	0.00
Benzo(b)fluoranthene	4/5-ring	5.80	0.0000635	0.23	0.01	0.02	0.00	0.01	0.00	0.00
Benzo(k)fluoranthene	4/5-ring	6.00	0.0000407	0.02	0.00	0.00	0.00	0.00	0.00	0.00
Benzo(e)pyrene		6.44	0.0000153	0.50	0.00	0.01	0.00	0.01	0.00	0.00
Benzo(a)pyrene	4/5-ring	6.04	0.0000373	nd	0.00	0.00	0.00	0.00	0.00	0.00
Perylene		6.25	0.0000234	nd	0.00	0.00	0.00	0.00	0.00	0.00
Indeno(1,2,3-c,d)pyrene	4/5-ring	7.00	0.0000044	nd	0.00	0.00	0.00	0.00	0.00	0.00
Dibenz(a,h)anthracene	4/5-ring	6.75	0.0000077	nd	0.00	0.00	0.00	0.00	0.00	0.00
Benzo(g,h,i)perylene	4/5-ring	6.63	0.0000101	nd	0.00	0.00	0.00	0.00	0.00	0.00
Total decalins				69.3	5.95	46.8	0.00	42.1	8.45	0.05
Total PAH (from naphthalene)				205	24.1	61.9	7.96	44.4	16.7	5.95
Modeled naphthalene compounds				9.19	13.5	35.0	7.00	22.5	10.6	4.48
Modeled 2/3-ring compounds				106	6.00	14.4	0.58	13.8	3.45	0.84
Modeled 4/5-ring compounds				4.83	0.37	0.56	0.00	0.46	0.11	0.11
Total modeled PAH (naphthalene-5 ring compounds)				120	19.8	49.9	7.58	36.8	14.2	5.43

PAH, polycyclic aromatic hydrocarbon; K_{ow}, octanol–water partitioning coefficient.

[a] The tissue concentrations are in ng/g, wet weight. The Station S-1 mussels were 89.4% moisture and had a lipid content of 8.15%, dry weight.

Table 3
Estimated water concentrations (ng/L) based on semi-permeable membrane device (SPMD) data[a]

	Modeling group	Estimated sampling constants		Example SPMD data Tampen S-1 (ng/SPMD)	Tampen stations			Ekofisk stations		
		Rate (Rs)	Time (days)		S-1 (ng/L)	S-5 (ng/L)	S-10 (ng/L)	S-4 (ng/L)	S-6 (ng/L)	R2 (ng/L)
Decalin		3.0	25	236	3.15	2.83	1.83	2.63	1.92	0.84
C1-decalins		6.6	28	427	2.31	2.04	0.57	3.76	1.86	1.21
C2-decalins		7.0	28	402	2.05	1.97	0.72	5.66	0.92	0.31
C3-decalins		7.0	28	340	1.73	1.94	0.85	3.57	0.00	0.00
C4-decalins		6.6	28	366	1.98	1.71	0.93	2.72	0.00	0.00
Benzo[b]thiophene		1.4	10	nd	0.00	0.00	0.00	0.00	0.00	0.00
C1-benzothiophenes		2.4	15	nd	0.00	0.00	0.00	0.00	0.00	0.00
C2-benzothiophenes		2.9	25	nd	0.00	0.00	0.00	0.00	0.00	0.00
C3-benzothiophenes		6.6	28	nd	0.00	0.00	0.00	0.00	0.00	0.00
C4-benzothiophenes		7.0	28	nd	0.00	0.00	0.00	0.00	0.00	0.00
Naphthalene	Naphthalenes	1.9	10	342	18.0	18.8	10.9	4.90	2.40	1.32
C1-naphthalenes	Naphthalenes	2.6	20	523	10.1	12.3	3.33	5.98	3.37	0.25
C2-naphthalenes	Naphthalenes	6.4	28	958	5.35	5.08	1.37	3.99	3.42	0.13
C3-naphthalenes	Naphthalenes	7.0	28	1580	8.06	5.86	1.52	3.47	3.21	0.20
C4-naphthalenes		7.0	28	1160	5.90	3.41	0.95	1.60	1.28	0.10
Biphenyl		2.7	20	83.5	1.55	1.90	0.71	0.81	0.63	0.14
Acenaphthylene	2/3-Ring	2.3	20	nd	0.00	0.00	0.04	0.00	0.00	0.00
Acenaphthene	2/3-Ring	2.7	20	12.5	0.23	0.34	0.10	0.16	0.18	0.04
Dibenzofuran		2.9	25	41.4	0.57	0.57	0.36	0.49	0.47	0.42
Fluorene	2/3-Ring	3.0	25	101	1.35	1.25	0.49	1.26	0.83	0.32
C1-fluorenes		7.0	28	345	1.76	1.38	0.40	1.30	1.03	0.18
C2-fluorenes		7.0	28	633	3.23	2.22	0.46	1.67	1.34	0.32
C3-fluorenes		6.8	28	686	3.60	2.03	0.79	0.71	0.49	0.19
Anthracene	2/3-Ring	5.8	28	nd	0.00	0.00	0.00	0.05	0.05	0.01
Phenanthrene	2/3-Ring	7.6	28	631	2.97	2.47	0.73	1.24	0.85	0.24
C1-phenanthrenes/anthracenes	2/3-Ring	7.0	28	1380	7.05	3.83	0.67	3.19	2.00	0.36
C2-phenanthrenes/anthracenes	2/3-Ring	7.0	28	1150	5.86	3.14	0.49	3.15	1.55	0.50
C3-phenanthrenes/anthracenes	2/3-Ring	6.6	28	287	1.55	1.97	0.27	2.23	0.78	0.19

C4-phenanthrenes/anthracenes		5.8	28	140	0.86	1.18	0.00	0.71	0.09	0.02
Dibenzothiophene	2/3-Ring	6.4	28	103	0.57	0.29	0.11	0.18	0.17	0.04
C1-dibenzothiophenes	2/3-Ring	7.0	28	340	1.73	0.75	0.21	0.68	0.55	0.12
C2-dibenzothiophenes	2/3-Ring	7.0	28	483	2.46	0.84	0.18	0.79	0.50	0.17
C3-dibenzothiophenes	2/3-Ring	6.8	28	170	0.89	0.52	0.11	0.61	0.23	0.10
C4-dibenzothiophenes		6.2	28	48.0	0.28	0.23	0.00	0.22	0.00	0.00
Fluoranthene	4/5-ring	7.2	28	53.1	0.26	0.87	0.40	0.32	0.25	0.45
Pyrene	4/5-ring	9.0	28	18.4	0.07	0.09	0.02	0.11	0.07	0.04
C1-fluoranthenes/pyrenes		7.0	28	48.8	0.25	0.56	0.06	0.34	0.13	0.08
C2-fluoranthenes/pyrenes		6.6	28	45.2	0.24	0.57	0.00	0.46	0.08	0.00
C3-fluoranthenes/pyrenes		6.0	28	35.0	0.21	0.42	0.00	0.45	0.00	0.00
Benz(a)anthracene	4/5-ring	6.4	28	7.26	0.04	0.04	0.02	0.03	0.02	0.01
Chrysene	4/5-ring	7.4	28	60.9	0.29	0.29	0.11	0.30	0.14	0.16
C1-chrysenes		6.2	28	54.2	0.31	0.23	0.03	0.44	0.07	0.03
C2-chrysenes		5.6	28	33.4	0.21	0.52	0.00	0.69	0.00	0.00
C3-chrysenes		4.2	28	nd	0.00	0.23	0.00	0.36	0.00	0.00
C4-chrysenes		2.6	28	nd	0.00	0.00	0.00	0.00	0.00	0.00
Benzo(b)fluoranthene	4/5-ring	5.6	28	9.31	0.06	0.07	0.03	0.06	0.02	0.03
Benzo(k)fluoranthene	4/5-ring	5.8	28	1.78	0.01	0.01	0.01	0.04	0.02	0.04
Benzo(e)pyrene		5.6	28	7.61	0.05	0.04	0.01	0.09	0.01	0.02
Benzo(a)pyrene	4/5-ring	6.4	28	0.34	0.00	0.01	0.00	0.01	0.00	0.01
Perylene		6.0	28	nd	0.00	0.01	0.00	0.00	0.00	0.01
Indeno(1,2,3-c,d)pyrene	4/5-ring	6.0	28	nd	0.00	0.02	0.02	0.02	0.00	0.00
Dibenz(a,h)anthracene	4/5-ring	4.0	28	nd	0.00	0.00	0.00	0.00	0.00	0.00
Benzo(g,h,i)perylene	4/5-ring	3.6	28	1.05	0.01	0.02	0.03	0.06	0.00	0.01
Total decalins				1770	11.2	10.5	4.89	18.4	4.70	2.36
Total PAH (from naphthalene)				11,600	85.9	74.4	24.9	43.2	26.2	6.27
Modeled naphthalene compounds				3400	41.5	42.0	17.1	18.3	12.4	1.91
Modeled 2/3-ring compounds				4660	24.7	15.4	3.40	13.5	7.69	2.10
Modeled 4/5-ring compounds				152	0.75	1.41	0.62	0.96	0.52	0.75
Total modeled PAH (naphthalene-5 ring compounds)				8210	66.9	58.9	21.1	32.8	20.6	4.75

PAH, polycyclic aromatic hydrocarbon; SPMD, semi-permeable membrane device; Rs, sampling rate.

[a] The SPMD data have not been corrected for SPMD blank/background concentrations.

The analytical methods used in this study were developed jointly by scientists at Battelle, National Oceanic and Atmospheric Administration (NOAA), and the National Institute of Standards and Technology (NIST) for trace-contaminant analysis of complex environmental matrices, and further refined by Battelle for detailed hydrocarbon characterization. The procedures have been described elsewhere (Durell et al., 2000; NOAA, 1998; Røe Utvik et al., 1999; US EPA, 1993), and are only summarized below. A rigorous quality assurance program was implemented to provide data of the highest quality. The program included processing an extensive set of laboratory quality control samples along with each batch of field samples, and monitoring the results against pre-established data quality objectives, to ensure that the analysis was in control (e.g., acceptable accuracy, precision, no laboratory contamination, and complete and representative data).

2.2.1. Blue mussel (M. edulis) tissue preparation

The mussel samples were shucked and the whole soft tissue homogenized with a stainless steel/Teflon Tissuemizer, and subsampled for extraction. Approximately 30-g, wet weight, of tissue was used for the analysis. The tissue was placed in a Teflon jar with sodium sulfate for extraction. Surrogate internal standard (SIS) compounds were added and the sample was macerated and serially extracted three times with a Tissuemizer using dichloromethane as the solvent. The extract was then concentrated using a combination of Kuderna–Danish and N-Evap nitrogen evaporation techniques, and purified by target compound specific alumina-column fractionation and high-performance liquid chromatography/gel permeation chromatography (HPLC/GPC). Tissue lipid concentration was determined using a sub-sample of the pre-purified extract. The purified extract was concentrated to approximately 0.5 mL, and spiked with recovery internal standard (RIS) compounds.

2.2.2. SPMD sample preparation

Excess algal material was documented and carefully wiped off the SPMDs with ChemWipes, and the SPMDs were placed in individual Teflon jars with a small amount of sodium sulfate. SIS compounds were added to the sample and the samples were serially extracted three times (>24 h, 12 h, and 6 h) with hexane. The extract was then concentrated using Kuderna–Danish and N-Evap nitrogen evaporation and purified by alumina column and HPLC/GPC techniques. The purified extract was concentrated to about 0.3 mL, and spiked with RIS compounds.

2.2.3. Instrumental analysis

Concentrations of the target individual organic compounds were determined by high-resolution capillary gas chromatography/mass spectrometry (HRGC/MS), with the detector operating in the selective ion monitoring (SIM) mode for optimum sensitivity and specificity; a Hewlett–Packard 6890/5973 GC/MS system was used. The GC was equipped with a 30-m DB-5 fused silica capillary column (0.25 mm ID and 0.25 μm film thickness) and a split/splitless injector (with electronic pressure control) operated in the splitless mode. The instrument was pre-tuned with perfluorotributylamine (PFTBA) each day, calibrated with a 5-point initial calibration consisting of the target compounds ranging in concentration from 0.005 to 5 ng/μL to establish and demonstrate the linear range of the analysis. The calibration was verified with a mid-level calibration check standard

analysis every 10 samples. Samples were quantified by the method of internal standards using the surrogate compounds as quantification internal standards to best represent the original field sample contaminant concentration.

2.3. Estimation of water concentrations from mussel/SPMD data

The data analysis included estimating the concentration of organic contaminants in the water based on the concentrations measured in the mussel and SPMD samples.

2.3.1. Estimating water-column concentrations from mussels

Concentrations of organic compounds in seawater were estimated from the mussel residue data as described by Neff and Burns (1996), with lipid fraction regression constants as derived by Pruell (Pruell et al., 1986). The calculation (Eq. (1)) is based on tissue bioaccumulation of non-polar organic compounds, the establishment of concentration equilibrium between the mussel tissue and the surrounding water, and uses measured tissue burden concentrations and tissue lipid fraction, as follows:

$$C_w = C_{t,obs}\ (L_{reg}/L_{obs})10^{-[A\log(K_{ow})+B]} \quad (1)$$

where, C_w = concentration of chemical in the water column (ng/L), $C_{t,obs}$ = concentration of chemical in the mussel tissue (ng/kg, wet weight), L_{reg} = the lipid fraction in the tissue used in developing the regression (0.0037), L_{obs} = the lipid fraction determined for the mussel tissue (g lipid/g tissue, wet weight), A and B = the slope function and intercept of the regression equation; the values used for mussels are +0.965 and −1.40, respectively (Neff and Burns, 1996; Pruell et al., 1986), log K_{ow} = the log octanol/water partition coefficient for the chemical.

2.3.2. Estimating water-column concentrations from SPMDs

SPMDs have been used widely to monitor concentrations of non-polar compounds in aquatic systems, primarily as a tool to determine relative concentration differences among sampling stations, either alone or in conjunction with caged bivalves (Axelman et al., 1999; Baussant et al., 2001; Hoefelt and Shea, 1997; Peven et al., 1996; Prest et al., 1992; Richardson et al., 2003). Methods have been developed for using SPMD concentration data to estimate the contaminant concentration in the water column. The general method described by Huckins et al. (1993) was used in this study (Eq. (2)), with adjustments to account for the water current based on Booij (Booij et al., 1998) and personal communications with Huckins and Booij.

$$C_w = C_{SPMD}/[(Rs \times F) \times t] \quad (2)$$

where, C_{SPMD} = concentration of chemical in SPMD (ng/SPMD), Rs = sampling rate (L/day), F = sampling rate (Rs) correction factor, to adjust Rs for actual water flow. Adjustments to base sampling rates are described below. t = sampling/uptake time (28 days; less for low log K_{ow} compounds).

Directly applicable sampling rates (Rs) have not been published for all compounds of interest in this study. A large set of PAH Rs values were published by Luellen and Shea (2002), but they were generated for water at a temperature of 25 °C and could not be used directly. Sampling rates appear to remain relatively constant between 2 and 13 °C, but increase substantially between 13 and 30 °C (Booij et al., 2003, 2000; Huckins et al.,

2000). It is unclear how the Rs values reported for 25 °C by Luellen would translate to the significantly cooler North Sea water temperatures, which were about 10 °C during the deployment period. Huckins et al. (1999) published Rs values for the 16 US EPA priority pollutant PAH at 10 °C, and the Rs values for those 16 compounds were used directly for the water concentration calculations. Using the published Rs values for the 16 priority pollutant PAH, the log K_{ow} (log octanol/water partition coefficient) values for these PAH, and the relationship between the log K_{ow} and the sampling rate of SPMDs, the following second-order polynomial equation was developed (Eq. (3)).

$$\mathrm{Rs} = -0.4823(\log K_{ow})^2 + 5.0326(\log K_{ow}) - 9.6163 \quad (r^2 = 0.746) \tag{3}$$

Using this derived equation, and the known log K_{ow} value for each compound, base Rs values were estimated for the 37 target compounds for which published Rs values could not be found. The log K_{ow} values used in this work are listed in Table 2, and are those judged to be most reliable based on a review of relevant publications (Huckins et al., 1999; Luellen and Shea, 2002; McGrath et al., 2001; Neff and Burns, 1996) and log K_{ow} estimation software (SRC, 1998), when published experimental values were not available (e.g., a few decalin and benzothiophene compounds).

Three adjustments to the Rs values were then considered; adjustments to reflect (1) the flow rate of the water in which the SPMDs were deployed, (2) water temperatures, and (3) biofouling of the SPMDs. These are all factors that have been described as having the potential to affect uptake rates (Booij et al., 2000, 2002, 2003; Huckins et al., 1999, 2000; Luellen and Shea, 2002; Richardson et al., 2002; Vrana and Schürmann, 2002). The published base sampling rates, and the base sampling rates estimated for additional compounds, are based on a flow rate of 1 cm/s and a water temperature of 10 °C. The average flow rate in the Tampen and Ekofisk Regions during the exposure periods was approximately 13 cm/s. Huckins and Booij have determined the following relationship between flow rate and sampling rates; flow rates of 0.03, 1, and 30 cm/s generated Rs values of 2.7, 3, and 8.7, respectively, given otherwise constant conditions. This relationship generates the following equation:

$$\mathrm{Rs} = -0.0038(\text{flow rate})^2 + 0.3132(\text{flow rate}) + 2.6906 \tag{4}$$

By entering a flow rate of 1 and 13 cm/s into this equation, the Rs value for 13 cm/s was determined to be 2.0 times higher than for 1 cm/s. This constant of 2.0 was then used to adjust the previously calculated Rs values (which were based on 1 cm/s) to 13 cm/s (i.e., F in Eq. (2) is 2.0). This flow rate based adjustment was only applied to boundary layer controlled compounds (compounds with log $K_{ow} > \sim 4.2$); it was therefore *not* performed on 11 compounds or compound classes (decalin, C0–C2 benzo[b]thiophenes, C0–C1 naphthalenes, biphenyl, acenaphthene, acenaphthylene, dibenzofuran, and fluorene) assumed to establish an SPMD-water column equilibrium concentration during the deployment period.

The water temperature was between 10 and 12 °C during deployment. Sampling rate increases with increasing water temperature, but the small deviation from 10 °C would not be expected to significantly impact the rate (Booij et al., 2000, 2003), so no adjustment was made for the temperature.

Biofouling of the SPMD membranes reduces the rate of contaminant uptake, and methods exist for adjusting the Rs value accordingly (Huckins et al., 2000). However, biofouling typically begins after 7–14 days in coastal water (Hoefelt and Shea, 1997; Huckins

et al., 2000) and occurs more slowly and less severely in colder, lower nutrient, offshore waters. Little, if any, biofouling was observed on the SPMDs after the 28 days of deployment in this study; therefore, biofouling was not expected to be a significant factor in the contaminant uptake and was not factored in to the calculations.

The SPMDs were deployed for 28 days; therefore, this was the sampling time (t in Eq. (2)) for boundary layer controlled compounds (compounds with log $K_{ow} > 4.2$). Sampling times estimated from uptake curves generated by Luellen and Shea (2002) were used for the 11 PAH listed earlier that were not under boundary controlled conditions; uptake rate curves for compounds not presented in Luellen and Shea (2002) were obtained from Luellen (pers. comm.). The time at the inflection point between the linear uptake part of the curve and the point of equilibration was used for these 11 compounds, even though it represented a time slightly beyond the linear portion of the curve (on which the uptake rate is based), because the SPMDs accumulate contaminants until the point of equilibration. Based on information from the uptake curves, the following sampling times were used for the 11 non-boundary layer compounds: 10 days for compounds with log $K_{ow} < 3.5$, 15 days for compounds with log K_{ow} 3.5–3.75, 20 days for compounds with log K_{ow} 3.75–4, and 25 days for compounds with log K_{ow} 4–4.25.

2.4. Water concentration estimation – using the DREAM model

Concentration fields were calculated for the produced water discharges in the two regions with the DREAM model developed by SINTEF, Trondheim, Norway (Reed et al., 2001); SINTEF also performed the modeling reported in this paper. The resulting time series of concentration fields can be accessed and presented for the geographic area of interest.

The model simulates transport, dilution, degradation, and general fate of chemicals released into the water from one or more sources simultaneously. DREAM includes a three-dimensional dispersion model that is able to simulate the spreading of contaminants as "particles" in three dimensions for a time-varying wind and current input. The "particles" are spread due to vertical and horizontal diffusion, and are also transported due to the currents. The concentration of the released components is estimated from the calculated "particle" density at various distances from the source. The modeling system consists of a near-field release model and a far-field transport model. The near-field release model is based on buoyant plume equations developed by Koh and Chang (1973) and Brandsma (Brandsma et al., 1980). The far-field model uses individual releases from the near-field plume to simulate the further transport and fate of contaminants in the water column. The model provides data based on total contaminant concentrations and does not distinguish between dissolved and particle bound contaminants.

The DREAM model uses actual measured produced water discharge volume and concentration data, discharge depth, physico-chemical compound data, and the local hydrodynamic and meteorological data to predict the dilution of the contaminants and concentrations in the ocean. For the survey in the Ekofisk Region, current fields from the actual period of the survey were obtained and used in the modeling. Meteorological information was not available for the Tampen Region for the period of the survey in this area, and approximate average information for that time of the year and that general area were therefore used.

3. Results and discussion

Target compound concentrations were determined in triplicate SPMD and mussel samples from each station. Excellent precision was achieved (generally less than 5% relative standard deviation in concentrations); therefore, average data for each station were calculated and used. Mussel Total PAH concentrations ranged from 20 to 2900 ng/g dry weight in the field deployed mussels, and SPMD Total PAH concentrations ranged from 600 to 8600 ng/SPMD; mussel Total PAH concentrations were above 1000 ng/g dry weight for deployments within 1 km of a discharge. Tables 2 and 3 present the complete PAH compound data for mussels and SPMDs from station S1 in the Tampen Region, as an example. The PAH in mussels and SPMDs deployed within 2 km of discharges was dominated by phenanthrene, fluorenes, naphthalenes, and dibenzothiophenes, and the alkylated compounds (e.g., C2- and C3-homologous) were detected at notably higher concentrations than the unalkylated, parent, PAH compound.

The water column concentrations were estimated using the mathematical approach previously described. A high, medium, and low concentration station from the two study regions were selected for closer analysis. The high station was located near a major oil platform discharge (near-field location, within 0.5–1 km); station S5 near the Troll B platform was chosen in the Tampen Region and station S4 near the Ekofisk 2/4K platform was used in the Ekofisk Region. The medium concentration station was located further away (intermediate distance, regionally influence location, within 5 km) from a major discharge. The low concentration station was from a reference location that was not expected to be influenced by regional discharges (about 80–90 km from produced water discharges); stations S10 (Tampen) and R2 (Ekofisk) were used to represent the general background for these parts of the North Sea.

3.1. Mussel- and SPMD-based estimated seawater concentrations

Table 2 summarizes estimates of concentrations of individual target compounds in water based on tissue residue data for mussels deployed at stations S1, S5, and S10 in the Tampen Region and stations S4, S6, and R2 in the Ekofisk Region. Table 3 summarizes the water concentration estimates based on concentrations in SPMDs deployed at the same stations. The constants used for the water concentration calculations are also presented in Tables 2 and 3, as are the mussel tissue and SPMD concentrations for one example location (Tampen station S1).

Tables 2 and 3 also summarize the total concentrations of the naphthalenes, 2/3-ring, and 4/5-ring classes of compounds that are used by the Norwegian regulatory authorities for produced water discharge management, with the compounds that are included in each of these classes indicated in the second column; these are also the compound class summations generated by the DREAM model. The sums of other selected groups of compounds are also presented (e.g., decalins and total PAH; these include all four measured alkyl homologue groups).

The SPMDs and mussels deployed near the platform discharges (within 1 km of the discharge), and at intermediate locations representing general regional impact (within 5 km), had a petrogenic contaminant profile. The compound composition was dominated by the naphthalenes, phenanthrenes, dibenzothiophenes, fluorenes, and decalins at these locations, with concentrations of the alkylated homologues similar to or higher

than the parent compound concentrations. The most water-soluble compounds (e.g., naphthalene), and trace levels of some pyrogenic compounds, were detectable at reference locations; naphthalene possibly originated from different petroleum sources, including produced water, and the higher molecular weight pyrogenic PAH likely mostly came from atmospheric transport and deposition of combustion-derived hydrocarbons from sources at sea and on land. Naphthalene is also a common laboratory contaminant, and was determined to be under control for these analyses (as were all PAH).

The composition of the PAH assemblage was different in the water than in the SPMD membranes and mussel tissue (Tables 2 and 3), reflecting differences in partitioning behavior of different hydrocarbons between ambient water and the mussel tissues or SPMDs. For instance, the 2/3-ring PAH concentrations were higher than the concentrations of naphthalenes in the mussel tissue and SPMDs from station S1 in the Tampen Region, but the naphthalenes were estimated to be present at about twice the concentration of the 2/3-ring PAH in the water column. The higher molecular weight, more hydrophobic, compounds with higher log K_{ow} values accumulate to higher concentrations in the tissue and SPMDs, relative to their concentrations in the water column. This is a reflection of the relationship between analyte hydrophobicity and bioaccumulation potential.

The individual compound concentrations were consistently low, although contaminant signals were clearly discernable. Some of the naphthalene and decalin compounds were estimated to be present at a concentration of 5–20 ng/L in the water column within 1 kilometer of the major platforms, while estimated concentrations of most other compounds were below 1 ng/L (Table 2 and 3). Fig. 3 summarizes the estimated water concentrations and distribution (based on mussel tissue residues) of the key classes of compounds at the three selected stations in the Ekofisk Region. The concentrations of the major produced water aromatic hydrocarbons (naphthalenes and 2/3-ring PAH) were clearly highest at station S4, which was closest to the major produced water discharge, and lowest at the reference location (station R2). The water concentrations that are estimated based on mussel (and SPMD) data indicate that the 2/3-ring PAH concentrations are about 40% the total PAH near the discharges, decrease to about 25% at the intermediate distant stations (1–10 km from discharges), and further decrease to 15% of the total PAH at background locations. The 4/5-ring PAH constitute a fraction of the total PAH; generally not more than 2% of the total PAH near the discharges. The naphthalenes are the most water-soluble of the aromatic hydrocarbons monitored and persist over a greater distance in the water column than the less soluble 2/3-ring compounds, and their contribution to the total PAH assemblage increases with distance from the platforms (from about 60% to about 80% of the total PAH). The more hydrophobic 2/3-ring PAH likely adsorb to organic matter and other suspended solids in the water column to a greater degree than the naphthalenes, and may settle with it to deeper water layers and to the sediment. The decalin compounds, which are present at high relative concentrations in produced water, decrease particularly rapidly with distance from the discharge, due to their low water solubility and affinity for particles and organic matter. Decalins are a useful indicator of produced water discharge. The concentrations of pyrogenic PAH (4/5-ring PAH) increase in relative amount away from the platforms (from about 1% to about 2% of the total PAH), as background concentrations of combustion related PAH become relatively more significant.

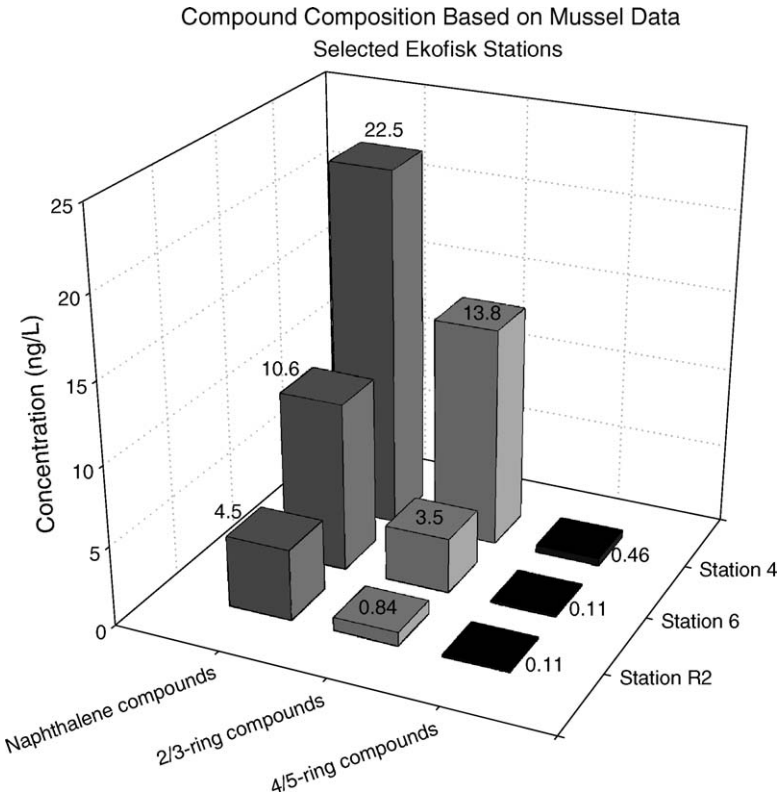

Fig. 3. Concentrations of the major compound classes at selected locations in the Ekofisk Regions – calculated using mussel (*Mytilus edulis*) data (ng/L).

The data have not been corrected for background/blank concentrations (Table 4). This is a particularly important consideration for the SPMD data. We have observed fluctuating batch-by-batch SPMD concentrations, particularly of naphthalenes and decalins, in the SPMDs; concentrations that may not be a concern for most users of SPMDs but do impact measurements of low- to sub-ng/L levels in North Sea waters. The SPMD blank levels are a reflection of compounds present in the membranes and lipid, not from contamination during sample collection or handling (''fresh'' SPMDs from the vendor had the same PAH concentrations as SPMD field blanks). These blank levels limited the usefulness of the SPMD data to stations near platform discharges. SPMDs with significantly lower blank levels have recently become available.

Mussel data should not be adjusted for the original tissue concentrations because the mussels equilibrate with the surrounding water concentrations (unlike SPMDs that steadily increase in concentration of most contaminants). In fact, the tissue concentrations were lower after deployment at several of the study stations than they were when collected from the mussel farm. The background/blank data in Table 4 indicate membrane blank levels (SPMDs) and laboratory blank results (mussels); concentrations comparable to these are likely included in the field sample data, in addition to the field-incurred amounts.

Table 4
Summary of modeled and measured water concentrations (ng/L)

	Naphthalenes			2–3 Ring PAHs			4–5 Ring PAHs			Total PAHs		
	Mussel	SPMD	DREAM	Mussel	SPMD	DREAM	Mussel	SPMD	DREAM	Mussel	SPMD	DREAM
Tampen Region stations												
S1	13.5	41.5	5.0	6.00	24.7	0.5	0.37	0.75	0.05	19.8	66.9	5.55
S1 (w. British sector)			42.7			15.0			0.30			58.0
S2	18.6	47.8	168	7.66	23.6	27.4	0.46	0.78	0.57	26.8	72.1	196
S2 (w. British sector)			187			38.3			0.75			226
S3	16.1	36.4	22.1	1.48	19.3	4.26	nd	0.63	0.17	17.6	56.3	26.5
S5	35.0	42.0	311	14.4	15.4	32.7	0.56	1.41	0.57	49.9	58.9	344
S6	6.85	27.9	5.37	1.96	20.9	0.90	0.16	1.28	0.07	8.97	50.1	6.35
S7	6.41	21.2	5.01	0.73	6.68	0.63	nd	0.48	0.05	7.14	28.3	5.69
S8	5.33	20.2	5.0	0.27	4.67	0.5	nd	0.59	0.05	5.60	25.5	5.55
S9	9.01	18.3	5.08	1.00	4.29	0.66	nd	0.49	0.05	10.0	23.1	5.80
S10	7.00	17.1	5.0	0.58	3.40	1.02	nd	0.62	0.07	7.58	21.1	6.09
Background/blank[a]	2.30	27.4	5.0	nd	2.76	0.50	nd	0.10	0.05	2.30	30.2	5.55
Ekofisk Region stations												
S1	17.7	12.8	20.1	9.27	11.3	2.10	0.32	0.85	0.07	27.3	25.0	22.3
S3	4.30	2.34	5.03	0.31	2.71	0.52	0.05	0.61	0.05	4.66	5.66	5.60
S4	22.5	18.3	29.6	13.8	13.5	2.60	0.46	0.96	0.07	36.8	32.8	32.3
S6	10.6	12.4	5.28	3.45	7.69	0.85	0.11	0.52	0.05	14.2	20.6	6.18
S7	6.63	3.32	5.66	1.02	3.47	0.54	0.04	0.46	0.05	7.69	7.25	6.25
S8	3.96	2.61	5.02	0.53	2.52	0.54	0.04	0.41	0.05	4.53	5.54	5.61
S9	5.48	3.34	5.61	0.98	4.05	0.67	0.06	0.56	0.05	6.52	7.95	6.33
S10	4.63	2.55	5.18	0.75	3.05	0.56	0.06	0.53	0.05	5.44	6.13	5.78
S11	4.00	3.35	5.35	0.99	4.18	0.62	0.05	0.93	0.05	5.04	8.46	6.02
R2	4.48	1.91	5.0	0.84	2.10	0.50	0.11	0.75	0.05	5.43	4.75	5.55
Background/blank[a]	1.70	4.01	5.0	nd	0.18	0.50	nd	0.10	0.05	1.70	4.29	5.55

PAH, polycyclic aromatic hydrocarbon; SPMD, semi-permeable membrane device; DREAM, dose-related risk and effect assessment model; Mussel, *Mytilus edulis*.

[a] The background/blank data are represented by laboratory method blanks (mussel data), field-blanks including the SPMD membrane (SPMD data), and generally accepted North Sea background levels (modeled data). Field blanks using the original mussel material are not representative of mussel background levels because the mussels equilibrate, up and down, with surrounding water concentrations. No data have been corrected for background levels. The modeled data background levels are North Sea background estimates and are incorporated into the model predictions.

3.2. Comparison of concentrations determined from field samples and from modeling

Table 4 presents the estimated water column contaminant concentrations at 10 stations in each of the Tampen and Ekofisk Regions; the table presents estimated concentrations based on mussels, SPMDs, and the DREAM model. The data are presented as the major contaminant groups used in the North Sea water column management regime; naphthalenes, 2/3-ring PAH, 4/5-ring PAH, and total PAH (the sum of the naphthalenes through 4/5-ring PAH groups). Fig. 4 presents the total PAH data.

3.2.1. Ekofisk data

The mussel, SPMD, and model-based estimated total PAH concentrations in ambient water are highly comparable for the stations in the Ekofisk Region, with the model predicting essentially the same or slightly lower concentrations than were estimated from

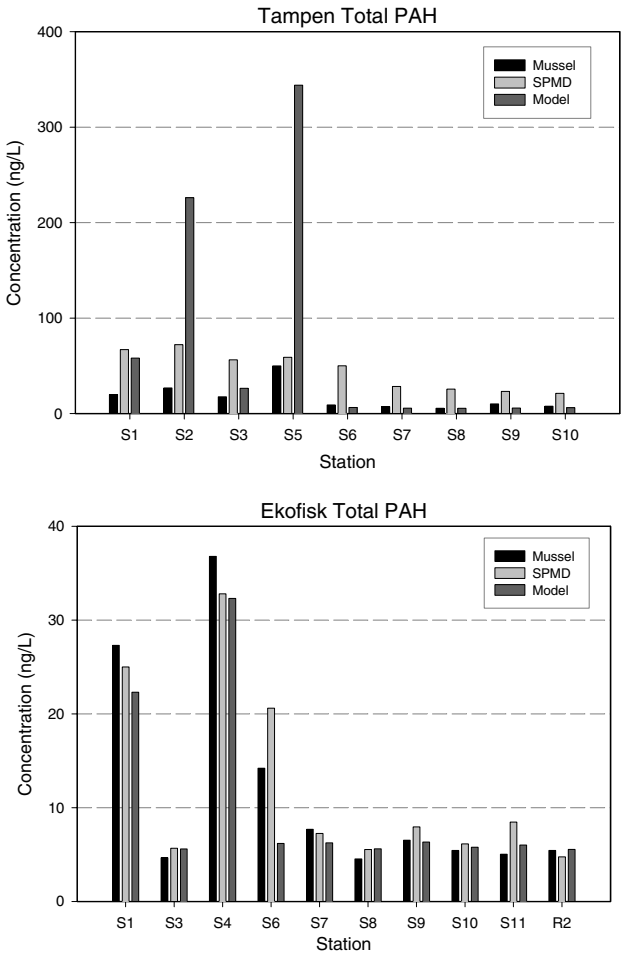

Fig. 4. Total polycyclic aromatic hydrocarbon (PAH) concentrations at sampling locations in the Tampen and Ekofisk Regions – data from mussel (*Mytilus edulis*) and semi-permeable membrane device (SPMD) field measurements and modeled data (ng/L).

the field samples. All methods yielded the highest concentrations for the stations closest to the major discharges (stations S1 and S4), and these stations had approximately 4–6 times higher concentrations than the background levels. The total PAH concentrations were 20–40 ng/L at the stations that were within 1 km of the platform discharges, and around 4–6 ng/L away from platform influence.

The naphthalenes concentration estimates for the Ekofisk Region were also consistent among the three methods (Fig. 5). There was greater variability for the less abundant 2/3-ring and 4/5-ring compounds. The total 4/5-ring PAH concentrations were consistently below 1 ng/L, with individual compound concentrations mostly below 0.1 ng/L, and some of the variability was likely due to the compounds being present near the limit of detection and the inherent sampling and analytical variability associated with that. Another factor is that the mussels and SPMDs capture any PAH present at sea, including from sources other than produced water (e.g., atmospheric deposition), while the model estimates the PAH only from produced water discharge and regional background. Background levels of 5, 0.5, and 0.05 ng/L were assumed and used in the modeling of naphthalenes, 2/3-ring PAH, and 4/5-ring PAH, respectively.

Most of the difference in the total PAH concentration estimates for the stations near discharges (stations S1, S4, and S6) can be attributed to the difference in the estimates for the 2/3-ring PAH. The mussel and SPMD data indicate that the concentrations of 2/3-ring PAH are about half the naphthalenes concentrations within 1 km of the discharge (station S4), while the model predicts the difference to be a factor of 10; the mussels/SPMDs appear to over-estimate the concentrations of the 2/3-ring PAH or the model is under-estimating the concentrations, or some combination of the two. The model predicts a naphthalene compound to 2/3-ring PAH compound ratio that is consistent with the concentration in the produced water discharge, suggesting the modeled results for the 2/3-ring PAH may be more accurate. However, many processes affect these compounds. The relative concentrations of the PAH may change once the contaminants enter the ocean due to compound-specific processes; the target PAH have different rates of evaporation, solubility, and degradation, and different affinity for organic matter and particles, all of which are factors that are difficult to accurately represent in a model. For instance, the more volatile naphthalenes may evaporate at a greater rate then the less volatile compounds following produced water discharge to the sea; produced water often is discharged at an elevated temperature (as much as 50–80 °C). This would result in a lower concentration of naphthalene relative to 2/3-ring PAH.

The log K_{ow} values used in the mussel-, SPMD-, and model-based water calculations are generally less reliable for the alkylated compounds than the parent PAH, and may result in unknown and different types of bias; the alkylated PAH contribute the most to the concentrations of naphthalenes and 2/3-ring PAH. Finally, the field-deployed SPMDs and mussels capture actual contaminants in the water column, regardless of sources, while the model predicts the concentrations resulting from the produced water discharge; any local sources of PAH (e.g., other waste discharge, platform runoff, vessels, cuttings piles in the shallow Ekofisk waters), other than produced water would not be accounted for with the model.

3.2.2. Tampen data

An important difference between the work in the Tampen and Ekofisk areas is that some of the Tampen area stations were, to a greater degree, influenced by tidal current

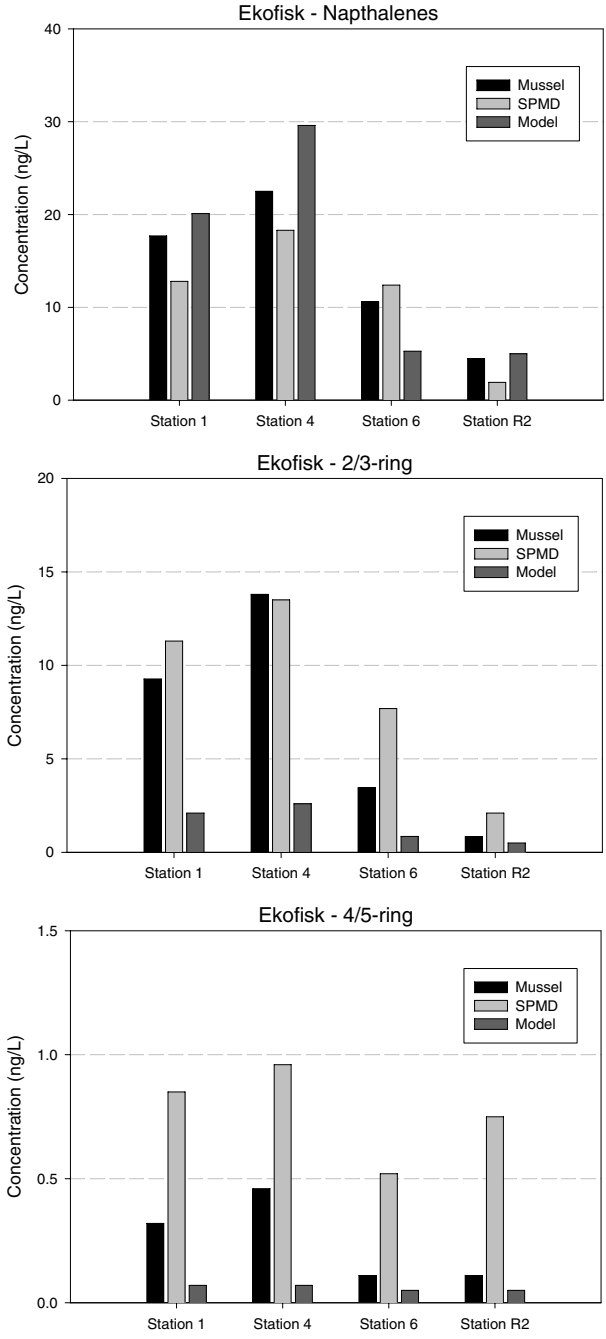

Fig. 5. Concentrations of the major compound classes at selected locations in the Ekofisk Regions – data from mussel (*Mytilus edulis*) and Semi-permeable membrane device (SPMD) field measurements and modeled data (ng/L).

fluctuations. The degree of tidal influence varies for different parts of the Tampen Region, and is particularly strong for stations located close to discharges (e.g., S2 and S5; 0.5 km from the discharge) where the plume is most concentrated. In the Ekofisk area the discharge plumes appear to be more uniformly and predictably dispersed (Fig. 6), and, importantly, none of the stations were closer than 1 km to the discharge. A tidally influenced plume will travel across a sampling buoy placed within its reach twice a day; the sampling devices may only be exposed to the plume a few hours a day and to a much lower contaminant concentration the rest of the day.

The mussel-, SPMD-, and model-based total PAH concentration estimates were less comparable for the stations in the Tampen Region than in the Ekofisk Region. The data indicate that the background/blanks associated with the SPMDs were quite variable and contributed 20–30 ng/L to the SPMD total PAH data (Table 4), making the SPMD data of less value.

The mussel-based and modeled data were more comparable for the stations away from direct produced water influence (e.g., S6 and S9), but the model predicted considerably higher concentrations than the mussel data for the stations close to produced water discharges (e.g., S2 and S5). The average total PAH concentrations were estimated to be 25–50 ng/L at the stations that were about 0.5 km from the platform discharges (S2 and S5) using the mussel data; the model predicted the concentrations to be about 200–350 ng/L. The model predicted about 7 times higher total PAH concentrations for station S2 (0.5 km from Statfjord) and station S5 (0.5 km from Troll) than was estimated with the mussel data.

The model actually predicted lower concentrations for station S1 than was measured using mussels. Station S1 was on the west side of and away from most influence from the major Statfjord and Gullfaks discharges. Station S1 was near the British sector where there are major production activities. When the DREAM model was re-run after including

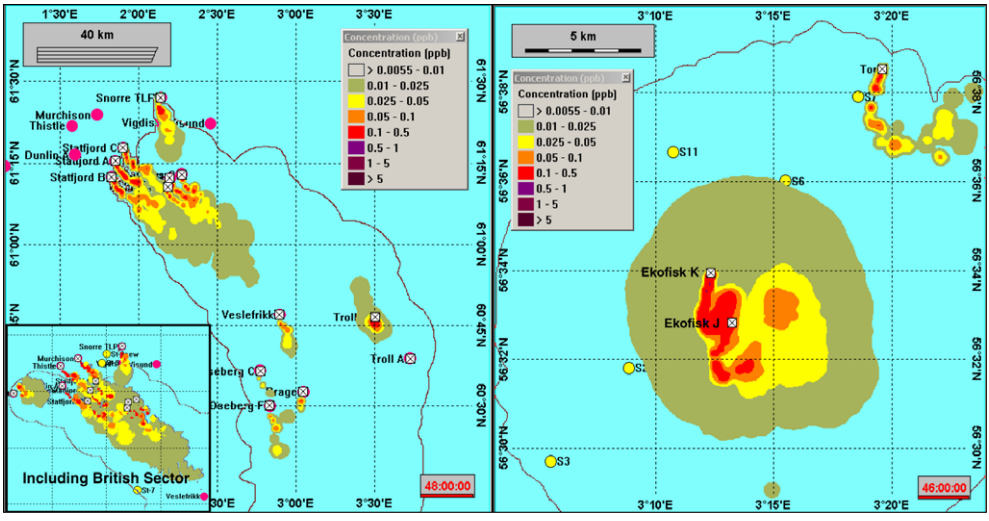

Fig. 6. Model output map presenting the total polycyclic aromatic hydrocarbon (PAH; naphthalenes through 5-ring PAH) concentrations in the Tampen (left) and Central Ekofisk (right) region. Major platform discharge locations are also indicated.

British sector discharges the estimated PAH concentrations at station S1 (and S2) increased significantly (Table 4, Fig. 6); the mussel data had reflected actual field concentrations, while the modeled results had under-estimated the concentrations by only including Norwegian sector discharges.

One reason for the higher modeled data compared to the field-measured data in the Troll area (station S5) could be that there was drilling activity near Troll during the deployment period, with discharge of drill cuttings, which could have increased the suspended solids in the water column; suspended solids could adsorb hydrocarbons and making them less available for concentration by mussels. The model predicts water column concentrations based only on produced water discharge, while the mussels reflect actual water column exposure. The impact of these drilling activities was confirmed with separate dissolved and particulate phase analysis of grab samples; at station S5, about 30% of the total PAH was associated with particulates while at most other locations it was about 10% (Røe Utvik et al., 1999).

Another reason for the discrepancy in the measured and modeled data for stations S2 and S5 could be the result of short-term exposure to a sweeping plume, and the methods not adequately accounting for relatively large and frequent fluctuations. This effect would be most pronounced at stations close to the discharge (like S2 and S5) where the plume is relatively small and more focused, where the time exposed to the plume may be short, and where there are sharp concentration gradients in the water column. Mussel tissue concentrations of hydrocarbons fluctuate with those of the surrounding water, reflecting continuous equilibration between the water and tissues. This results in an accumulation of contaminants during exposure to the plume and a depuration of contaminant when not exposed to the plume. There is a lag in this process, and equilibrium is not fully reached with exposure concentrations that fluctuate greatly and frequently. In a recent laboratory-based experiment, we compared the contaminant uptake of mussels exposed to a constant concentration (24 h/day) to that of a fluctuating regime (2×45 min/day; a sweeping plume effect). The hydrocarbon concentration in the water in the constant and "plume" exposure was more than a factor of 100 higher than in the "clean" water in the fluctuating regime test. After about 10 days the mussels in the constant exposure test had 10 times higher naphthalenes concentrations than in the fluctuating exposure test, but the phenanthrenes concentrations were only a factor of two higher (Table 5); studies have shown that most PAH reach an equilibrium in the mussel tissue in less than 20 days of exposure (Peven et al., 1996; Axelman et al., 1999; Richardson et al., 2003). The naphthalenes appear to respond more rapidly to fluctuating concentrations than higher molecular weight compounds. The mussel tissue concentrations in the fluctuating exposure were similar to, or slightly lower than, the starting concentration after 10 days. This suggests that the 1.5 h/day exposure to contaminated water does affect the tissue concentrations, but the 22.5 h/day of "clean" water is dominating the effect. It appears that an exposure of 1–2 h or less a day to the elevated concentration would not result in an overall increase in tissue burden. It is, however, not clear what duration and frequency of exposure is needed for notable overall accumulation to occur. It is also not clear how these conditions compare to those at stations S2 and S5 in the Tampen Region. It is, however, clear that tidal effects on the discharge plume can have a significant impact on the bioaccumulation of PAH. The bioaccumulation kinetics under fluctuating concentration conditions is not well documented; therefore, it is unclear how closely the mussel tissue burden concentrations represent the time-average exposure. It is likely that the results calculated using mussels

Table 5
Mussel (*Mytilus edulis*) tissue accumulation of naphthalene and phenanthrene compounds during constant and fluctuating concentration exposure

	Exposure water concentration[a] (μg/L)		Mussel tissue concentration (ng/g, dry wt.)	
	"High" concentration	Average concentration	Day 0	Day 9 and 12 average
Constant exposure[a]				
Naphthalenes (C0–C2)	2.34	2.34	147	1470
Phenanthrenes (C0–C2)	0.052	0.052	282	360
Fluctuating exposure[a]				
Naphthalenes (C0–C2)	2.35	~0.2	147	142
Phenanthrenes (C0–C2)	0.059	~0.005	282	197

[a] The exposure water concentration is the concentrations the test mussels were exposed to for 24 h a day in the constant exposure experiment and for 2×45 min a day in the fluctuating exposure experiment (The mussels were exposed to "clean" water the remaining 22.5 h/day, with a the water exchanging completely in a few minutes).

under-estimate the near-platform concentrations in the Tampen Region, considering the limited time the mussels were exposed to the elevated plume concentrations.

The water column concentration calculations based on mussel data may be under-estimating the average concentration, and the DREAM model may also be less accurate and possibly over-estimate the concentrations by exaggerating the fluctuations in contaminant concentrations in a highly tidally influenced environment. As illustrated in Fig. 7, the "swings" in concentrations predicted by the DREAM model appeared higher for some locations than expected. The near-field component of the DREAM model is being further developed to improve the accuracy near discharges. Major tidal influences clearly complicate model predictions of contaminant concentrations in the water column, as well as

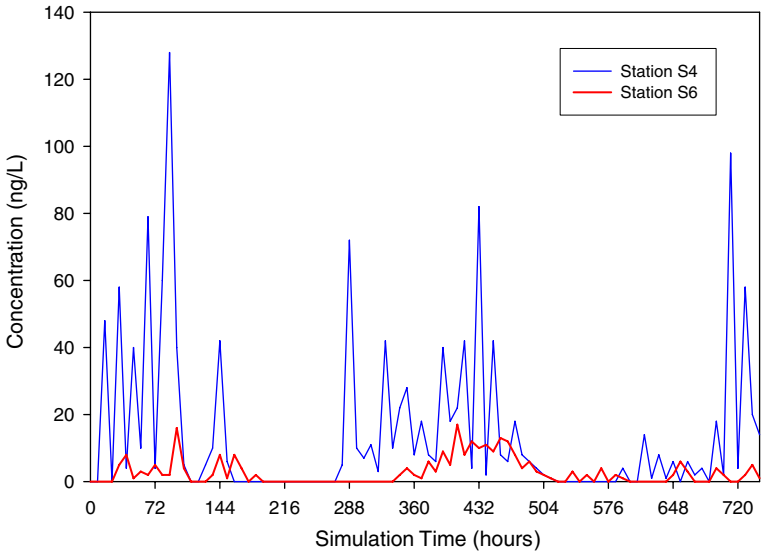

Fig. 7. Time series of modeled total polycyclic aromatic hydrocarbon (PAH; naphthalenes through 5-ring PAH) Concentrations at Station S4 and Station S6 in the Ekofisk Region.

estimations of water concentrations based on accumulations in mussel tissue. This fluctuating contaminant concentration also compromises the reliability of calculations based on SPMD data, although the addition of performance reference compounds (PRCs) should improve the soundness of SPMD-based estimates (Booij et al., 2002; Huckins et al., 2002).

3.2.3. Factors impacting mussel-based, SPMD-based, and modeled concentration estimates

It is clear that the estimated mussel-, SPMD-, and model-based water column concentrations each have their inherent limitations and reliability (Booij et al., 2000, 2002; Huckins et al., 2000; Luellen and Shea, 2002; Richardson et al., 2002, 2003), and understanding influencing factors is important for the use of the data, and for making improvements in future investigations.

Mussels capture primarily the dissolved phase non-polar organic compounds, but also some particle-bound contaminants that can be retained in the gills or digestive diverticula or desorbed from the particles and absorbed (assimilated) from the gut of the animal (Neff, 2002). The SPMDs capture almost exclusively dissolved phase non-polar organics. Consequently, mussels tend to represent the total accessible component of the exposure, while SPMD represent the dissolved contaminants that have the potential to accumulate in lipid. If the water column contains elevated concentrations of suspended solids and dissolved/particulate organic matter (e.g., microplankton, detritus, suspended sediments, or oil droplets), the contaminants may adsorb to or complex with this organic matter, depending on a variety of physico-chemical processes (e.g., the type and size of the solids or droplets, contact time, the log K_{ow} of the compound etc.; Neff, 2002), and quite different results may be obtained for mussels and SPMDs. Some particle associated contaminants may be accumulated by the mussel, and some may travel through the animal completely adsorbed to particles, some of which may be measured in a chemical analysis if still present on the gills or in the gut. The mussel-based water concentration estimates are based on the assumption that all the PAH in the tissues have been assimilated into tissue lipids and are in equilibration with the dissolved phase in the ambient water; unassimilated particle-bound PAH on the gills or in the gut produce an over-estimate of the dissolved PAH concentration in the ambient water. Careful depuration of the animals prior to analysis can remove most of such contamination, but there is then a risk of also reducing tissue concentrations of assimilated PAH, particularly of the less hydrophobic hydrocarbons. The mussels equilibrate more rapidly than SPMDs with the water concentrations, and may be more susceptible to water column fluctuations.

The mussel-based water calculations rely on accurate lipid fraction data. Different lipid determination methods can generate very different results. Randall et al. (1991) determined that four lipid determination methods, each with different organic solvent extractants, generated lipid content data for blue mussels that ranged from 0.67% to 1.42%, wet weight; for bluefish liver, the difference between the highest and lowest value was a factor of 3.1. The importance of this measurement, and establishing it's applicability to the calculations developed by Pruell et al. (1986) and Neff and Burns (1996), should not be under-estimated.

Furthermore, published log K_{ow} values vary widely, and there is not always consensus on their representativeness; the appropriate log K_{ow}s need to be identified and used consistency in the various estimations (mussel, SPMD, and model-based). The uncertainty in log K_{ow} values is particularly great for the alkylated PAH. Log K_{ow} values are based on the phase distribution of a compound between octanol and water, and octanol may not

be the perfect surrogate material to represent the solubility of PAH in different kinds of animal tissue lipid (Connell, 1993).

Factors that impact the rate of contaminant uptake in SPMDs were discussed earlier. One potentially important factor to consider in the accumulation of organic compounds in and on SPMDs is the presence of biological material on the membranes. Visible algal growth is typically wiped off the outside of the membrane, and the degree to which this is performed successfully can affect the results; organic material tends to adsorb organic compounds, and compounds with higher log K_{ow}s (e.g., 2/3-ring PAH) preferentially more so than those with lower log K_{ow}s (e.g., naphthalenes). However, a non-visible organic film can also build up on the outside of SPMDs, concentrating organic contaminants in a similar way. Direct analysis of such an SPMD can result in data that are quite different than would be obtained with a "clean", film-free, SPMD. Another important factor to consider for the use of SPMDs in trace-level monitoring is the background levels in the SPMDs themselves. It appears that the SPMD are now available with lower levels, but it is important to test and verify that any background present in the SPMDs does not affect the data quality objectives of the study.

The model, like the mussels, does not distinguish between dissolved and adsorbed contaminants; it makes a prediction of the water column concentration based on the total concentrations in the produced water discharge. In fact, the model includes all contaminants associated with the discharge, including particle-bound PAH and dispersed oil droplets that would not be bioaccumulated and assimilated by mussels or other biota. The model is highly dependent on accurate physico-chemical constants and fate-transport data, and appropriate weighting of the various input parameters; these data need to be kept up-to-date to minimize bias. For instance, the available physico-chemical data for the alkylated PAH is generally less reliable than the data for the non-alkylated PAH, and uncertainties with the alkylated PAH compounds will have a great impact on the results because these are the major PAH in produced water. Assumptions about the behavior of alkylated PAH that are based on extrapolations from non-alkylated PAH can cause significant error.

Another important consideration when using and comparing modeled results to other data are that the model prediction is based on produced water discharge volumes and concentrations from periodic discharge monitoring. The discharge volumes are measured quite frequently, but the analysis of complete produced water contaminant concentrations is only performed once or twice a year (total petroleum content is monitored regularly). Discharge volumes and concentrations vary, and it is important, to the extent possible, to ensure that the model input information represents the study period (e.g., the 28 days of mussel and SPMD deployment, if such a comparison is performed). Finally, the model is driven by produced water discharge, and would not account for other possible releases associated with the oil and gas production platforms, or unrelated sources of contamination (e.g., ships and atmospheric deposition) that contribute to the PAH in seawater and that are captured using the mussels and SPMDs.

4. Summary and conclusions

Similar concentrations of produced water originating PAH were estimated using caged blue mussels, SPMDs, and the DREAM model for the Ekofisk Region of the North Sea. These are three independent methods of determination, resulting in a high level of confidence in the highly comparable results. The total PAH concentrations in the upper water

column were estimated to be 20–40 ng/L within 1 km of the major produced water discharges in the Ekofisk Region, and declined to background levels of about 4–6 ng/L at a distance of 5–10 km from the source. The PAH in the water column consisted of approximately 60% naphthalenes and 40% 2/3-ring PAH within 1 km of the discharge, and the relative proportion of 2/3-ring PAH declined away from the source while the relative amounts of naphthalenes and 4/5-ring PAH increased due to higher solubility (naphthalenes) and sources other than produced water (4/5-ring PAH).

The PAH concentrations were less comparable among the different methods for the Tampen Region; particularly for the near-discharge stations where the tidal influence results in a distinct "sweeping" plume. The model predicted higher average concentrations than measured in the field for the stations near discharges (i.e., within the discrete signal of the plume); similar concentrations were estimated by the different methods for the more distant stations. The higher concentrations, and greater uncertainty in the results, at the near-discharge stations in the Tampen Region is partly because those stations were closer to the discharge ($\sim$0.5 km, as opposed to $\sim$1 km for the Ekofisk Region near discharge stations). The model may not fully represent the contaminant dispersion near discharges. By the same token, the concentration estimates based on mussel and SPMD data also probably do not fully account for the effects of fluctuating water column concentrations, and may be underestimating the average concentrations. The near-platform concentrations in the Tampen Region may therefore quite possibly be in the 50–100 ng/L range; a range between the measured and modeled values.

Both blue mussels and SPMDs have proven to be rugged and effective in concentrating trace levels of non-polar organic contaminants from the water column, providing time-integrated contaminant information. Blue mussels are particularly useful for providing a direct measurement of contaminant bioavailability; the mussel is a living organism that is accumulating contaminants, which are then measured. SPMDs are an indirect measure of bioaccumulation potential, and preferentially sample the dissolved phase contaminants. Mussels, if collected from a clean area, usually have little PAH, while SPMDs historically have had blank contamination issues for a number of the compounds at the trace concentrations investigated in this work. Other effects that can confound the analysis of SPMD data (e.g., factors that affect uptake rates, and fluctuating concentrations) can be reduced by the use of PRC compounds, as described by Booij et al. (1998, 2000, 2002) and Huckins et al. (2002).

The application of mussels, SPMDs, and the model to an environment with highly fluctuating water column concentrations needs to be more fully investigated, and the findings incorporated into future concentration estimates. The behavior of the plume can be characterized and predicted, and it should be possible to conduct controlled field and laboratory based studies to provide the necessary information to further refine the methods.

The field-based mussel and SPMD water column estimates were, for the most part, relatively consistent with model predictions. Potential causes for the observed discrepancies have been discussed. All three methods identify a small zone of elevated PAH concentrations associated with produced water discharges to the Norwegian sector of the North Sea. Although hydrocarbons were detected over a wide area, this was primarily a reflection of ultra-sensitive analytical methods, rather than concentrations likely to cause ecologically important biological effects. The field-based work supports the DREAM model as a promising tool for produced water discharge and impact management, although field-based studies should continue to validate the model and ensure that it is applicable to new

environments. The deployment of mussels and SPMDs, and modeling, complement each other and are a powerful combination of tools for monitoring, assessing, and managing the potential impact of discharge from offshore oil and gas production activities.

Acknowledgements

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