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Oil well produced water discharges to the North Sea. Part II: Comparison of deployed mussels (*Mytilus edulis*) and the DREAM model to predict ecological risk

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Abstract

Large volumes of water often are produced with oil and gas from offshore platforms. The produced water is separated from the oil and gas and either reinjected into a deep formation or discharged to the ocean. The Norwegian oil and gas industry advocates ecological risk assessment as the basis for managing produced water discharges to the North Sea. In this paper, we compare estimates of ecological risks to water-column communities based on data on hydrocarbon residues in soft tissues of blue mussels deployed for a month near offshore platforms and based on predictions of the Dose related Risk and Effect Assessment Model (DREAM). The study was performed near produced water discharges to the Tampen and Ekofisk Regions of the Norwegian Sector of the North Sea. Because polycyclic aromatic hydrocarbons (PAH) are considered the most important contributors to the ecological hazard posed by produced water discharges, comparisons made here focus on this group of compounds. The mussel approach is based on predicted environmental concentrations (PECs) of individual PAH, estimated from PAH residues in mussels following deployment for a month near several produced water discharges, and predicted no effects concentrations (PNECs) based on a K_{ow} regression model. In the DREAM method, PECs for three PAH fractions

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are estimated in the three-dimensional area around produced water discharge with the DREAM model. PNECs for each fraction are based on the chronic toxicity of a representative PAH from each fraction divided by an assessment factor to account for uncertainty in the chronic value. The mussel method gives much lower estimates of ecological risk than the DREAM method. The differences are caused by the much lower PNECs used in DREAM than derived from the regression model, and by the lower concentrations of aqueous PAH predicted by DREAM than estimated from PAH residues in mussel tissues. However, the two methods rank stations at different distances from produced water discharges in the same order and both identify 2- and 3-ring PAHs as the main contributors to the ecological risk of produced water discharges. Neither method identifies a significant ecological risk of PAH in the upper water column of the oil fields. The DREAM model may produce an overly conservative estimate of ecological risk of produced water discharges to the North Sea.

Keywords: Bioaccumulation; Toxicity; Mussels; Model; Risk assessment; Petroleum hydrocarbons; Polycyclic aromatic hydrocarbons

1. Introduction

Produced water usually is the waste generated in largest volume during production of oil and gas from offshore oil and gas wells. Most produced water is fossil water (formation water) that has accumulated over millions of years with the fossil fuels in geologic formations deep in the earth. Produced water also may contain some surface water that has been injected into the formation for enhanced oil recovery. Produced water reaches the surface from natural oil seeps world-wide and during production of oil and gas from a well. The material produced from a well often is a mixture of crude oil, natural gas, and produced water. Produced water contains a wide variety of chemicals that have been dissolved or dispersed from the fossil fuels and the geologic reservoir containing the formation water (Neff, 2002).

Produced water generated on offshore platforms may be sent by pipeline to shore for treatment and disposal, reinjected, or treated and discharged to the ocean, depending on local environmental regulations and available technology. Produced water usually is treated to remove dispersed oil and sometimes salts before reinjection or on-shore or offshore disposal. The regulatory limit for total petroleum hydrocarbons in produced waters discharged offshore in the North Sea is 40 mg/L (Ayres and Parker, 2001). Produced water that has been treated to remove dispersed oil may contain a wide variety of chemicals in solution or colloidal suspension, in addition to petroleum hydrocarbons, including inorganic salts (essentially the same as those in natural seawater, but usually at different ion ratios), several metals and metalloids, and a wide variety of organic chemicals (Neff, 2002). The organic chemicals include low molecular weight organic acids, phenols, unidentified polar compounds, petroleum hydrocarbons, related S-, N-, and O-substituted hydrocarbons, and several industrial chemicals (additives) used in various phases of production. The chemicals of greatest environmental concern in produced water destined for ocean disposal, because of their potential for bioaccumulation and toxicity, are metals and hydrocarbons, particularly those dissolved in the water phase. Produced water metals usually dilute to background concentrations in seawater within a few meters of the discharge point and so usually don't contribute to the ecological risk of produced water discharges to the ocean (Neff, 2002).

In 2000, the Norwegian oil and gas industry introduced ecological risk assessment as the basis for managing produced water discharges to the North Sea. An ecological risk assessment integrates measured or estimated levels of exposure to a chemical contaminant and measured or predicted injury to valued ecosystem components to characterize the risk (potential hazard) of the chemical to natural populations of the valued ecosystem components. A model system, the Dose related Risk and Effect Assessment Model (DREAM), was developed for this purpose (Reed et al., 2001). DREAM calculates an environmental impact factor (EIF), which is a measure of the volume of seawater that contains high enough concentrations of produced water chemicals to exceed a pre-determined risk criterion. The EIF provides a regional-scale, quantitative estimate of the potential ecological risks to marine organisms of produced water discharges (Johnsen et al., 2000).

The primary function of the EIF is to serve as a management tool, assisting the operator to identify and select cost-effective measures to reduce potential environmental risk. Due to its nature, the EIF does not characterize the environmental conditions of the recipient, but identifies the risk of environmental harm from the discharge. Therefore, an accurate quantitative target for reducing the EIF is not relevant, but a reduction in the EIF implies a reduction in the potential environmental risk from the specific produced water discharge.

An EIF has been determined for each of the oil and gas fields in the Norwegian Sector of the North Sea. These EIFs were included in the ‘Zero Discharge Report’ prepared by the operators in the Norwegian sector in 2000. The Zero Discharge Report formed the basis for the industry’s strategy and actions to reach zero environmentally harmful discharge of produced water by the year 2005.

The oil industry established an objective of zero harmful discharge in response to regulatory goals established by the Norwegian government in the White Paper No. 58 “Zero Discharge Report” issued in 1998 (SFT, 1999; Johnsen et al., 2000). The objective of the zero harmful discharge strategy is to identify environmentally harmful discharges or chemical components of discharges so that cost-effective, technology-based approaches can be developed to treat or dispose of the discharge to remove its adverse impacts to the total environment (Frost et al., 2002). The EIF is intended to be a basis for a cost-effective approach to region-wide management of produced water discharges to the Norwegian Sector of the North Sea (Grini et al., 2002). The EIF assists the operator in reaching the zero harmful discharge goal by identifying toxic constituents of produced water so that they can be removed or treated.

In parallel with the industry’s development of the EIF, the Norwegian State Pollution Control Agency (SFT) initiated a new environmental monitoring program for ocean discharges from offshore oil and gas operations to the Norwegian Sector of the North Sea. Monitoring studies addressing the potential environmental impact of produced water discharges on a regional scale have been completed for two North Sea regions, the Ekofisk Region and the Tampen Region. The Tampen environmental monitoring study was performed in 1997–1998 as the first survey that applied the methods and principles described in the revised Norwegian monitoring guidelines (SFT, 1999). The results of this study served as the basis for developing the official Norwegian strategy for monitoring ecological risks of produced water discharges from offshore production facilities to water column communities. The results of the Tampen monitoring study have been summarized in several papers (Johnsen et al., 1998; Røe Utvik, 1999; Røe Utvik et al., 1999; Røe Utvik and Johnsen, 1999). Durell et al. (2004) and Durell et al. (2000) described the field monitoring programs and summarized the results of the Ekofisk monitoring study.

As a part of these studies, environmental risk assessments were performed for selected petroleum hydrocarbons in produced water, both by the DREAM/EIF model and by assessing the ecological risk from estimated concentrations of hydrocarbons in the water column, derived from tissue residues in deployed mussels. This paper is a comparison of these two approaches for estimating the environmental risk of produced water discharges to the North Sea.

2. Methods

2.1. The Tampen and Ekofisk monitoring studies

The Tampen Region is located in the north-central part of the North Sea, including parts of both the Norwegian and United Kingdom Sectors (Fig. 1). The density of offshore production platforms is high in the region, including some of the largest oil fields in the North Sea. Discharges of produced water in the Tampen area represent approximately

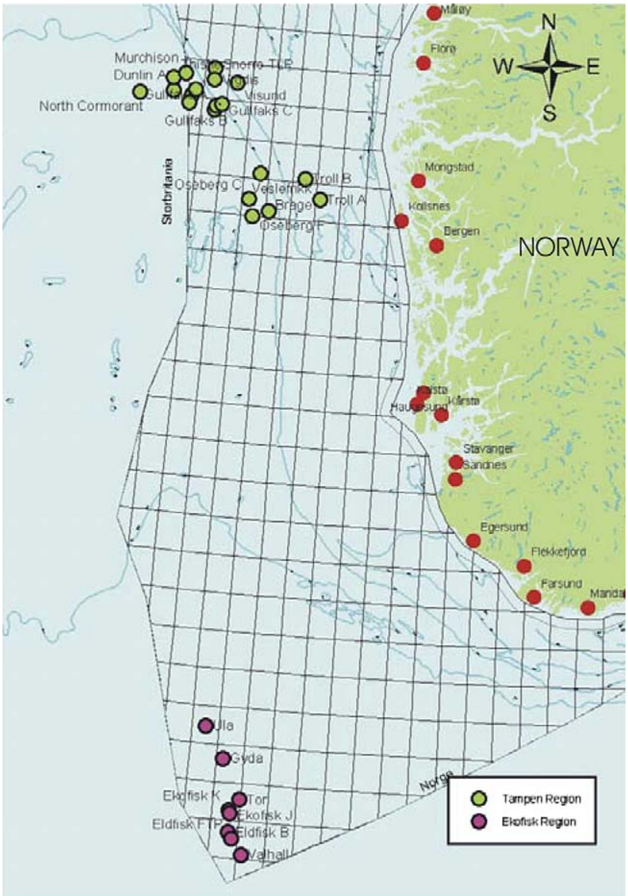

Fig. 1. Map of Norwegian Sector of North Sea showing Tampen and Ekofisk Oil and Gas Production Areas.

70% of the total discharge volume to the North Sea, estimated at 288 million m^3 in 1998 (Garland, 1998). More than 183,000 m^3/day of treated produced water is discharged to the North Sea from platforms in the Norwegian part of the Tampen Region. An estimated 120 million m^3 of produced water was discharged to the entire Norwegian Sector in 2000 (OLF, 1997).

The Ekofisk Region is located in the southernmost part of the Norwegian sector of the North Sea (Fig. 1). It is the oldest oil production area in the Norwegian Sector and, like the Tampen region, parts are shared with the UK Sector. The volume of produced water discharged from platforms in the Norwegian part of the Ekofisk Region is less than 10% of that to the Tampen Region. A regional environmental monitoring survey was performed in the Ekofisk region in 1999 (Durell et al., 2000).

An objective of these water column environmental monitoring surveys was to verify the predicted environmental concentrations (PECs) of produced water chemicals estimated by DREAM. Prior to the sampling surveys, produced water trajectories and dilutions were modeled for the region, and the sampling locations were designated to depict the concentration gradients predicted by the model. The concentrations of produced water compounds were measured in the region by several sampling and analytical methods. This paper relies on data for concentrations of polycyclic aromatic hydrocarbons (PAH) and other selected petroleum hydrocarbons in blue mussel (*Mytilus edulis*) deployed for a month at different distances from platforms; a companion paper (Durell et al., 2006) includes a description of the sampling and analytical methods and a comparison of the mussel and semi-permeable membrane device (SPMD) strategies for monitoring concentrations of organic contaminants in surface waters near offshore produced water discharges. The risk assessment comparison presented in this paper focuses on concentrations and potential ecological risks of PAH in surface waters of the Norwegian Sector of the North Sea.

2.2. Environmental risk assessment based on field monitoring data

This ecological risk assessment of produced water is based on a comparison of exposure concentrations of PAH, selected cyclic alkanes (decalins), and heterocyclic compounds (dibenzothiophenes) in the receiving waters to toxicity threshold concentrations. Concentrations of these produced water chemicals in ambient seawater from the sampling stations (the predicted environmental concentrations: PEC) were estimated based on concentrations in tissues of mussels. The concentration of each analyte in water was estimated from the mussel tissue residue data by the equation (Neff and Burns, 1996):

$$C_{\mathrm{w}} = C_{\mathrm{t,obs}}(L_{\mathrm{reg}}/L_{\mathrm{obs}})10^{-[\mathrm{a}\ \log(K_{\mathrm{ow}})+\mathrm{b}]}$$

where C_{w} is the concentration of chemical in water in equilibrium with mussel tissue (μg/L); $C_{\mathrm{t,obs}}$ is the concentration of chemical in mussel tissue (ng/g wet wt); $L_{\mathrm{reg}}$is the lipid fraction in the tissue used in developing the regression (0.0037); L_{obs} is the lipid fraction in the mussel tissue (g lipid/g tissue, wet weight); The constants, a and b = the slope function and intercept, respectively, of the regression equation; the values used for mussels are +0.965 and −1.40, respectively (Pruell et al., 1986); $\log K_{\mathrm{ow}}$ = the log octanol/water partition coefficient for the chemical.

The predicted no effect concentration (PNEC) describing the threshold toxic concentration of each chemical, was estimated by a regression model of the relationship between the acute toxicity and K_{ow} of the target chemicals. There are limited acute and chronic toxicity data available for individual petroleum hydrocarbons and marine animals. McCarty et al. (1992), Di Toro et al. (2000), and others have shown that there is a linear relationship between the log of the median lethal concentration (LC_{50}) to aquatic organisms and the $\log K_{ow}$ of nonpolar organic chemicals that exhibit toxicity by nonspecific narcotic action. The relationship can be described by a linear regression of log LC_{50} (mM/L) against $\log K_{ow}$ for each nonpolar organic compound.

A search of the EPA Aquatic Toxicity Information Retrieval (AQUIRE, 1997) database identified more than 300 values for the acute toxicity (median lethal concentration: LC_{50}) of aromatic hydrocarbons to freshwater and marine invertebrates and fish. LC_{50} concentrations greater than the aqueous solubility of the hydrocarbons were rejected (Neff et al., 2005). Suitable aquatic toxicity data were found for 25 aromatic hydrocarbons. Log geometric mean acute toxicity values (in mM/L) for the aromatic hydrocarbons were regressed against $\log K_{ow}$. The regression has a high correlation ($r^2 = 0.885$) and the form:

$$\text{Log LC}_{50}(\text{mM/L}) = -1.162 \log K_{ow} + 2.496$$

where K_{ow} is the octanol/water partition coefficient; log K_{ow} values for hydrocarbons were obtained from Mackay et al. (1992) and Neff and Burns (1996). This equation was used to estimate the acute toxicity of each PAH analysed in the mussel samples.

The PNEC was estimated by dividing the acute toxicity value by an acute/chronic ratio (ACR) of 25, the most conservative value recommended by the European Center for Ecotoxicology and Toxicology of Chemicals (ECETOC) for chemicals other than metals and pesticides (Länge et al., 1998).

The PEC for each target analyte in water at each sampling station was divided by the PNEC for that chemical to obtain a hazard quotient (HQ). Because the toxicity of petroleum hydrocarbons to aquatic receptors is thought to be by nonspecific narcotic action (McCarty et al., 1992; Di Toro and McGrath, 2000), the toxicities of individual hydrocarbons or hydrocarbon fractions are approximately additive (Warne et al., 1989; Van Wezel et al., 1996). HQs for all the target organic chemicals in receiving waters can be summed to produce a hazard index (HI), which is equivalent to the total hazard of the target hydrocarbons.

2.3. Environmental risk assessment with DREAM

Environmental risk assessment with DREAM also is based on the PEC/PNEC principle as defined by the European Union (EU) in a Technical Guideline Document (TGD) (EC, 1996). However, DREAM represents a modification of the TGD method that accounts for the complex mixture of chemicals in produced water and differences in their fates and toxicities in the marine environment (Johnsen et al., 2000). In DREAM, the chemical composition of produced water is represented by several chemical groups, each representing a class of chemicals with similar physical, chemical and biological properties. Produced water chemicals were divided into 10 groups of naturally-occurring organic compounds and metals, and seven groups of produced water additives (Johnsen et al., 2000). Monocyclic aromatic hydrocarbons, PAH, related heterocyclic aromatic compounds, and sometimes one or more metals, are considered the major toxicants in produced water (Neff, 2002); they are the compounds used most frequently in DREAM to estimate the EIF. The aromatic hydrocarbons are divided into four groups, representing the monocyclic aromatic hydrocarbons (benzene, toluene, ethylbenzene, and xylenes: BTEX), naphthalenes, other 2- and 3-ring PAH, and 4- and 5-ring PAH. Each of these groups is represented in the risk model by a single compound with environmental properties representative of those for the whole group. Johnsen et al. (2000) described the criteria for the selection of the representative chemicals.

Although BTEX is abundant in produced water (Røe Utvik, 1999; Neff, 2002), it is lost rapidly from the water column, mainly by evaporation, following ocean discharge of produced water (Terrens and Tait, 1996). Thus, BTEX was not included in the monitoring studies. The 4- and 5-ring PAH, because of their low concentrations in crude oil (Kerr et al., 1999) and low aqueous solubilities, usually are present at very low concentrations in produced water that has been treated to meet the regulatory limit of 40 mg/L total petroleum hydrocarbons. However, they are highly bioaccumulative and toxic to marine organisms (Baussant et al., 2001a,b; Neff, 2002). Despite their relatively high toxicities, they contribute little to the marine toxicity of produced water because of their low concentrations in produced water and in surface waters of the study areas.

Durell et al. (2006) describe the input data requirements for modelling, including produced water discharge locations, produced water discharge rates and compositions, local hydrodynamic conditions, and the locations of the different sampling/modelled sites for the two regions. For each sampling site, the predicted environmental concentrations (PECs) of the three PAH groups, averaged over 30 days, were extracted from the model. For this comparison, DREAM was programmed to produce a three-dimensional, time variable concentration field (the PEC) for each of the three produced water PAH groups, plus total PAH, as input to the PEC/PNEC estimation (Reed et al., 1996; Reed et al., 2001). The natural background concentration of each chemical group in surface seawater of the two North Sea areas was included in the calculations. Background concentrations were derived from analytical data for mussels from the reference stations (Durell et al., 2006). The background concentrations used in this study for naphthalenes, other 2- and 3-ring PAH, and 4- and 5-ring PAH were 5, 0.5, and 0.05 ng/L (parts per trillion), respectively. Grid size of the model was set to 500 m × 500 m × 10 m, meaning that the entire modelled areas were subdivided into 2.5×10^6 m^3 compartments for mean PEC determination. In practice this implies that the PECs do not vary within the boundaries of each compartment.

The concentration in the water column of the PAH from produced water is visualized as a regional, time variable, three-dimensional concentration field in which the actual concentration of each fraction for a particular geographic point can be read from the graphic output. Thus, a direct comparison with PAH concentrations measured in the monitoring study is possible when the actual meteorological and hydrodynamic data for the monitoring period are applied in the modeling.

Risk assessment modeling in the Ekofisk area was based on hydrodynamic and meteorological data for the actual sampling period (May 1999). Produced water discharges in the area are well characterized (Table 1), and each discharge point (platform) was assigned a specific produced water profile with respect to composition, discharge volume, and location.

Detailed information on produced water composition was available only for platforms in the Norwegian portion of the Tampen Region (Table 1). Discharges from the UK Sector of the Tampen Region probably affect the concentrations of PAH in the Norwegian Sector. Because produced water composition data were not available for the UK portion of the Tampen Region, the relevant discharge sources in the UK part of the Tampen area were not included in the modelling. However, a test run was carried out, in which average PAH concentrations from the Norwegian produced water discharges were applied to UK platforms. The results of this exercise showed that UK discharges could increase PAH

Table 1
Characteristics of produced water discharges from platforms in the Tampen and Ekofisk regions of the Norwegian Sector of the North Sea

Platform	Discharge volume (m^3/day)	Discharge depth (m)	Average concentration (mg/L)		
			Naphthalenes	2-3 Ring PAHs	4-5 Ring PAHs
Tampen region					
Statfjord A	28,200	15	1.29	0.149	0.003
Statfjord B	21,400	20	1.26	0.216	0.004
Statfjord C	24,500	20	0.90	0.086	0.001
Gullfaks A	15,700	18	0.85	0.071	0.001
Gullfaks B	24,800	20	1.20	0.129	0.002
Gullfaks C	19,400	28	0.99	0.097	0.001
Veslefrikk	7400	6	1.40	0.129	0.002
Troll A	3.7	20	0.48	0.009	0.000
Troll B	19,100	20	1.43	0.118	0.005
Snorre TLP	12,100	15	1.59	0.390	0.005
Oseberg C	4560	15	1.42	0.197	0.006
Oseberg FS	2510	19	1.11	0.111	0.003
Brage	3270	1	1.16	0.139	0.006
Total Volume	183,000				
Ekofisk region					
Ekofisk 2/4 K	3,300	22	0.47	0.046	0.0005
Ekofisk 2/4 J	1,990	39	1.05	0.066	0.0007
Eldfisk 2/7 B	255	12	0.58	0.042	0.0005
Eldfisk 2/7 A	167	3	0.87	0.091	0.0010
Tor	1520	6	0.25	0.012	0.0002
Valhall	255	not available	0.23	0.010	0.0001
Ula	1270	0	3.59	0.230	0.0052
Gyda	2900	0	0.50	0.040	0.0006
Total Volume	11,700				

PAH: polycyclic aromatic hydrocarbon.

concentrations by less than 10% in the western part of the Tampen region (near the sector line between UK and Norway). Due to a lack of hydrodynamic and meteorological data for the sampling period, dilution modelling in the Tampen region was based on a typical May scenario, taken from the year 1990.

Risk assessment in DREAM is performed by comparing the PEC from the dilution modeling to the PNEC for the chemical groups in the geographic area being modeled. The risk is presented as a time variable, three-dimensional risk map, in which the PEC/PNEC ratio, called the risk characterization ratio (RCR) in DREAM, is estimated for any geographic point and any time for the modeling period. The risk map displays the total RCR (sum of RCR contributions from each group of chemicals) in the recipient as water volumes representing different RCR levels.

An RCR for total PAH was obtained by summing the RCRs for the three PAH subgroups. Thus, it is possible to compare the total RCR calculated by DREAM to the HI calculated from measured environmental data. Modeling estimates the EIF for a produced water discharge by calculating the water volume in which the RCR exceeds 1.0. An RCR or HI greater than 1.0 indicates that the modeled or estimated contaminant concentrations are high enough in the ambient water to possibly represent a hazard to local marine plants and animals.

Table 2
Predetermined predicted no effect concentration (PNEC) values for naphthalenes and other polycyclic aromatic hydrocarbon (PAH) groups included in the environmental impact factor (EIF; Johnsen et al., 2000; Frost et al., 2002)

Group	Compounds	Representative	Assessment factor	PNEC value (ppb)	Reference
Naphthalenes	Naphthalene, C_1–C_3 alkyl homologues	Naphthalene	10	2.1	Caldwell, Calderone & Mallon et al., 1977
2–3-Ring PAH	Compounds in the EPA 16 PAH list with 2–3 rings, and dibenzothiphene, and C_1–C_3 alkyl homologues	Phenanthrene	10	0.15	Savino & Tanabe, 1989
4–5-Ring PAH	Compounds on the EPA 16 PAH list with 4–5 rings	Benzo(*a*)pyrene	100	0.05	Trucco, Engelhardt & Stacey, 1983

EPA: Environmental Protection Agency.

In DREAM, the naphthalenes are represented by naphthalene, phenanthrene represents the other 2- and 3-ring PAH, and benzo(*a*)pyrene represents the 4- and 5-ring PAH (Table 2). PNECs for the three PAH groups were derived from the results of a comprehensive literature review of aquatic toxicity data for the different chemicals and the application of the principles described in the TGD (Johnsen et al., 2000; Frost et al., 2002). The toxicity data used to derive PNEC values have been evaluated critically. Differences in toxicity of hydrocarbons among representative species at different trophic levels and acute as well as chronic data have been considered in the PNEC determination. The PNEC for a particular chemical was estimated by dividing the lowest available acute or chronic toxicity value by an assessment factor, as required in the TGD (EC, 1996). The value of the assessment factor applied is determined by the availability and the quality of the toxicity data for the chemical of concern. The lowest assessment factor of 10 is applied for chemical compounds having high quality chronic toxicity data at all the three trophic levels (algae, crustaceans, and fish).

The highest assessment factor of 1000 is used for determination of PNEC for compounds with only acute toxicity data available in accordance to the TGD guidance (EC, 1996). In general, the quality of the toxicity data for most 3–5-ring PAH is relatively poor (the exception is phenanthrene); because of low solubility, saturated solutions of many of the 4- and 5-ring PAH are not acutely toxic (Neff, 2002). However, high quality toxicity data are available for some of the lower molecular weight 2- and 3-ring PAH. Table 2 summarizes the PNECs for the PAH groups included in this risk characterization, assessment factors, and index compounds chosen to represent each group.

3. Results and discussion

3.1. Produced water discharges

More than 10 times as much produced water is discharged to the North Sea from the Norwegian portion of the Tampen Region than from the entire Ekofisk Region, most of which is in the Norwegian Sector (Table 1). Concentrations of PAH are similar in produced waters from both regions. Total PAH concentrations in the produced waters are below 2 mg/L (parts per million); more than 90 percent of the PAH in the produced waters are naphthalenes (naphthalene and C_1–C_4-naphthalenes). The produced water contains only traces of 4–5-ring PAH (Røe Utvik, 1999).

3.2. *Environmental risk assessment based on field monitoring data*

3.2.1. *Hydrocarbons in Mussel Tissues*

Mussel cages at three stations in the Ekofisk region and one station in the Tampen region were severely damaged or destroyed during the deployment period and live mussels could not be recovered from them. Concentrations of total target hydrocarbons (PAH, decalins, and dibenzothiophenes) in soft tissues of mussels that had been deployed for approximately one month at the remaining 12 stations in the Ekofisk region range from 90.5 to 6377 ng/g dry wt (parts per billion); mussels from the remaining nine stations in the Tampen field contain 18.1 to 9286 ng/g total target hydrocarbons (Table 3). No benzothiophene or alkylbenzothiophenes were detected in mussel tissues. These low molecular weight heterocyclic compounds are present at trace or nondetectable concentrations in the produced water from the two regions (Røe Utvik, 1999; Durell et al., 2000), and have relatively low K_{ow}s, explaining their lack of bioaccumulation in mussel tissues.

Table 3
Measured concentrations of total polycyclic aromatic hydrocarbons (PAHs) decalins, and heterocyclic compounds in tissues of mussels (*Mytilus edulis*), estimated concentrations in water, and hazard indices (HI) at sampling stations in the Ekofisk and Tampen Regions in the Norwegian Sector of the North Sea

Field/station	Distance from discharge (km)	Mussels (ng/g dry wt)	Water (μg/L)	HI
Tampen				
ST1	2 U[a]	2,580	0.030	0.01469
ST2	0.5 D[b]	3,450	0.042	0.01840
ST3	10 D	182	0.019	0.00087
ST5	0.5 D	9290	0.109	0.04457
ST6	10 D	634	0.010	0.00344
ST7		44.0	0.007	0.00013
ST8		18.1	0.006	0.00006
ST9		63.0	0.010	0.00026
ST10		57.5	0.008	0.00020
Ekofisk				
S1	0.5 U	6380	0.057	0.02191
S3	5 U	90.5	0.005	0.00027
S4	0.5 D	8630	0.086	0.03297
S6	5 D	2710	0.025	0.00852
S7	10 D	231	0.008	0.00067
S8	20 D	100	0.005	0.00027
S9	5 P[c]	257	0.007	0.00089
S10	20 P	141	0.006	0.00047
S11	5 P	276	0.005	0.00080
S12	20 P	100	0.005	0.00030
S13	50	255	0.008	0.00082
R2	90	189	0.006	0.00055

[a] Upstream of nearest discharge relative to the dominant residual current direction.
[b] Downstream of nearest discharge relative to the dominant residual current direction.
[c] Direction of nearest discharge perpendicular to dominant residual current flow.

Mussels deployed within 0.5 km of the nearest produced water discharge (Ekofisk Stations S1 and S4 and Tampen Stations 2 and 5) contain the highest concentrations of target hydrocarbons. Because tidal current direction in both Ekofisk and Tampen follows an elliptical path during the tidal cycle, mussels deployed at 0.5 km upcurrent, relative to the dominant residual current direction of the nearest discharge contain only slightly lower concentrations of hydrocarbons than mussels that were deployed 0.5 km downcurrent from the nearest discharge. Hydrocarbon residues in mussel tissues decline with distance from the nearest produced water discharge but are higher in mussels deployed at all distances downcurrent than in those deployed at similar distances upcurrent or perpendicular to the dominant current direction.

The most abundant target hydrocarbons in tissues of the most heavily contaminated mussels (deployed 0.5 km downcurrent from a discharge) are decalins, followed by phenanthrenes, and then naphthalenes (Table 4). The most abundant 4–6 ring PAH are C_1–C_3-fluoranthenes and pyrenes and C_1- and C_2-chrysenes.

Most mussels from reference stations or stations more than a few kilometers from the nearest platform do not contain detectable concentrations of decalins in their soft tissues. Two samples from stations distant from the Ekofisk discharges contain traces of decalin but no alkyldecalins. These results indicate that the decalins, because of their high vapor pressures and K_{ow}s and low aqueous solubilities (Ran et al., 2002), may either evaporate to the atmosphere or adsorb rapidly to suspended particulate matter following discharge of produced water and sink with the particles to the bottom. The most abundant PAH in mussels from stations more than a few kilometers from the nearest produced water discharge are alkylphenanthrenes (Ekofisk Region) or alkylnaphthalenes (Tampen Region). These differences may reflect differences in the composition of the produced water discharged in the two fields (Røe Utvik, 1999). These decalin and PAH compositions in tissues of mussels deployed within about 10 km of platforms resemble those in produced water and indicate that the tissue hydrocarbons probably were derived primarily from produced water discharges.

Mussels deployed at greater distances from platform discharges may derive their body burdens of PAH from a combination of produced water and effluents from motor vessels in the area, and from combustion sources (Neff, 2002). This hypothesis is supported by the observation that concentrations of fluoranthene, pyrene, and chrysene are higher than those of their alkyl homologues (typical of a combustion source) in the tissues of mussels from the more remote stations.

3.2.2. Estimated hydrocarbon concentrations in the water column

Concentrations, estimated from the mussel tissue residue data by the regression of Neff and Burns (1996), of total target analytes range from 0.005 μg/L to 0.11 μg/L in surface waters of the two fields, (Table 3). Neff and Burns (1996) showed a good correlation between measured and estimated (based on concentrations in mussel tissues) concentrations of PAH in waters of Prince William Sound, AK, after the *Exxon Valdez* oil spill.

By comparison, the average measured concentrations of total dissolved plus particulate PAH (10 parent PAH) in surface waters of the North Atlantic Ocean and Mediterranean Sea are 0.00063 and 0.00105 μg/L, respectively (Lipiatou et al., 1997). Concentrations of total PAH (sum of 15 parent compounds) in waters of the Baltic Sea range from 0.0005 to 0.014 μg/L (Witt, 1995). Surface waters of Chesapeake Bay (USA) contain 0.0025 to 0.091 μg/L total PAH (Gustafson and Dickhut, 1997). Thus, the range of estimated PAH concentrations in surface waters near produced water discharges in the North Sea are in the higher part of the range of measured concentrations in other coastal and offshore waters.

Table 4
Estimation of the hazard indices (HI) for total decalins, polycyclic aromatic hydrocarbons (PAHs), and heterocyclic compounds in surface water from Station S4, approximately 0.5 km downcurrent from a produced water discharge in the Ekofisk area, Norwegian Sector, of the North Sea

Chemical	Concentration in mussel tissue (ng/g wet wt)	Estimated concentration in water (PEC) (μg/L)	Hazard quotient (HQ)
Decalin	12.94	0.00550	0.00024
C1-decalins	80.61	0.01409	0.00163
C2-decalins	205.73	0.01478	0.00456
C3-decalins	179.31	0.00530	0.00440
C4-decalins	198.29	0.00241	0.00541
Naphthalene	1.68	0.00451	0.00002
C1-naphthalenes	4.15	0.00367	0.00006
C2-naphthalenes	28.19	0.00821	0.00050
C3-naphthalenes	68.30	0.00613	0.00141
C4-naphthalenes	55.60	0.00205	0.00128
Biphenyl	1.00	0.00083	0.00001
Dibenzofuran	0.60	0.00030	0.00001
Fluorene	2.09	0.00093	0.00003
C1-fluorenes	15.28	0.00117	0.00031
C2-fluorenes	39.05	0.00180	0.00081
C3-fluorenes	31.43	0.00048	0.00076
Anthracene	1.19	0.00024	0.00002
Phenanthrene	12.77	0.00305	0.00021
C1-phenanthrenes/anthracenes	64.69	0.00341	0.00132
C2-phenanthrenes/anthracenes	106.54	0.00276	0.00235
C3-phenanthrenes/anthracenes	96.11	0.00089	0.00244
C4-phenanthrenes/anthracenes	34.19	0.00013	0.00098
Dibenzothiophene	1.57	0.00045	0.00002
C1-dibenzothiophenes	11.43	0.00112	0.00020
C2-dibenzothiophenes	26.53	0.00063	0.00058
C3-dibenzothiophenes	24.97	0.00035	0.00057
C4-dibenzothiophenes	11.90	0.00007	0.00030
Fluoranthene	1.79	0.00008	0.00004
Pyrene	3.83	0.00018	0.00008
C1-fluoranthrenes/pyrenes	11.66	0.00028	0.00025
C2-fluoranthenes/pyrenes	19.90	0.00024	0.00046
C3-fluoranthenes/pyrenes	16.29	0.00007	0.00044
Chrysene	9.55	0.00018	0.00020
C1-chrysenes	15.38	0.00009	0.00039
C2-chrysenes	19.48	0.00006	0.00054
Benzo(*b*)fluoranthene	1.20	0.00001	0.00003
Benzo(*k*)fluoranthene	0.38	0.00000	0.00001
Benzo(*e*)pyrene	2.99	0.00001	0.00008
Benzo(*g*,*h*,*i*)perylene	0.70	0.000002	0.00002
Hazard Index (HI)			0.0330

Only hydrocarbons that were detected in one or more mussel tissue samples are included.
PEC: predicted environmental concentrations. Mussel: *Mytilus edulis.*

3.2.3. Estimated Hazard of Produced Water Chemicals in the Water Column

Published values of $\log K_{ow}$ were used to estimate the acute toxicity to marine organisms of all the target decalins, PAH, and heterocyclic compounds detected in one or more mussel samples (Table 5). Estimated acute toxicities of hydrocarbons increase (LC_{50}s decrease) with increasing $\log K_{ow}$ from 4890 μg/L for naphthalene to 0.64 μg/L for indeno(1,2,3-*cd*)pyrene. Chronic toxicities, estimated by application of an acute/chronic ratio of 25, range from 196 μg/L to 0.03 μg/L.

Table 5
Log octanol–water partitioning coefficient (K_{ow}) and estimated acute and chronic toxicity of polycyclic aromatic hydrocarbons (PAHs) frequently found in oil well produced water

PAH	$\log K_{ow}$	Acute toxicity	Chronic toxicity (PNEC)
Decalin	4.2	572	22.9
C1-decalins	4.6	216	8.65
C2-decalins	5.0	81.0	3.24
C3-decalins	5.4	30.1	1.20
C4-decalins	5.8	11.1	0.45
Naphthalene	3.37	4,890	196
C1-naphthalenes	3.87	1,420	56.9
C2-naphthalenes	4.37	410	16.4
C3-naphthalenes	4.9	108	4.33
C4-naphthalenes	5.3	40.2	1.61
Biphenyl	3.9	1,420	57.0
Acenaphthylene	4.00	1,060	42.5
Acenaphthene	3.92	1,350	54.0
Dibenzofuran	4.12	863	34.5
Fluorene	4.18	726	29.0
C1-fluorenes	4.97	95.1	3.81
C2-fluorenes	5.20	55.4	2.22
C3-fluorenes	5.70	15.6	0.62
Anthracene	4.54	297	11.9
Phenanthrene	4.46	368	14.7
C1-phenanthrenes/anthracenes	5.14	64.4	2.58
C2-phenanthrenes/anthracenes	5.46	29.4	1.17
C3-phenanthrenes/anthracenes	5.92	9.16	0.37
C4-phenanthrenes/anthracenes	6.32	3.34	0.13
Dibenzothiophene	4.38	471	18.9
C1-dibenzothiophenes	4.86	140	5.62
C2-dibenzothiophenes	5.50	27.2	1.09
C3-dibenzothiophenes	5.73	15.6	0.63
C4-dibenzothiophenes	6.1	6.17	0.25
Fluoranthene	5.22	54.7	2.19
Pyrene	5.18	60.9	2.44
C1-fluoranthrenes/pyrenes	5.5	27.6	1.11
C2-fluoranthenes/pyrenes	5.80	13.2	0.53
C3-fluoranthenes/pyrenes	6.28	3.88	0.16
Benz(*a*)anthracene	5.91	9.75	0.39
Chrysene	5.61	21.8	0.87
C1-chrysenes	6.14	5.59	0.22
C2-chrysenes	6.43	2.72	0.11
Benzo(*b*)fluoranthene	5.80	14.5	0.58
Benzo(*k*)fluoranthene	6.00	8.47	0.34
Benzo(*a*)pyrene	6.04	7.61	0.30
Indeno(1,2,3-*c*,*d*)pyrene	7.00	0.64	0.03
Dibenz(*a*,*h*)anthracene	6.75	1.26	0.05
Benzo(*g*,*h*,*i*)perylene	6.63	1.72	0.07

Acute and chronic toxicity values are μg/L (ppb).
PNEC: predicted no effects concentrations.

The high estimated acute and chronic toxicities (low LC_{50}s) for decalins are caused by their high $\log K_{ow}$s. Le Roux (1977) reported that growth of mussel larvae is reduced by 20% during exposure to 10 mg/L decalin (essentially a saturated solution), suggesting that decalin, like most alkanes, has a lower than predicted toxicity to aquatic organisms. Decalin and other saturated hydrocarbons have a lower aquatic toxicity than aromatic hydrocarbons with a similar K_{ow} (Battelle, 2000); saturated hydrocarbons may be metabolized rapidly in mussel tissues, reducing their net bioaccumulation and toxicity. The estimated acute toxicities of the other target compounds are in good agreement with published acute toxicities of aromatic hydrocarbons to freshwater and marine animals and with values estimated by others by similar methods (Neff, 1979, 2002; Di Toro et al., 2000).

The estimated concentration in surface waters of each target analyte (the PEC, Table 4) was divided by its estimated chronic toxicity (the PNEC, Table 5) to obtain a hazard quotient (HQ) (Table 4). Comparison of the HQs for all target analytes provides an indication of the relative contribution of different chemicals to the estimated hazard, as indicated by the sample HI, for surface waters near a produced water discharge. The most important contributors to the toxicity of the surface water at Station S4, 0.5 km downcurrent from a produced water discharge in the Ekofisk area (Table 4) and Station ST5 0.5 km from a discharge in the Tampen Field, the two stations with the highest HI values, are C_1–C_4-decalins and C_2- and C_3-phenanthrenes. As discussed above, the HQs for the decalins may be overestimates. Parent and C_1- and C_2-phenanthrenes and naphthalenes are the main contributors to the HIs at stations more than about 2 km from the produced water discharges where decalin concentrations usually are below the analytical method detection limit. Alkyl phenanthrenes are considered the main contributors to the chronic toxicity of weathered oil and aqueous effluents from oil operations (Hawkins et al., 2002; Neff, 2002; Oikari et al., 2002).

All HI values for surface waters of the Ekofisk and Tampen Regions are well below a value of 1.0, indicating little or no ecological risk from target hydrocarbons in produced water (Table 3). HIs range from 0.0001 to 0.001 at most stations remote from the produced water discharges to 0.033 at Station S4, 0.5 km downcurrent from a high-volume produced water discharge in the Ekofisk Field, and 0.045 at Station ST5, 0.5 km downcurrent from a high-volume discharge in the Tampen Field (Table 3).

HIs also were estimated for the 3 DREAM PAH fractions (Table 2) and total PAH. The PEC for each fraction was estimated as the sum of the estimated water concentrations (based on mussel residue data) of all the PAH in each fraction. The PNECs were the chronic values (Table 5) for the PAH in each fraction. For example, the HI for the naphthalenes fraction was calculated as:

$$\mathrm{HI}_{\mathrm{naphs}} = \sum \mathrm{PEC}_{\mathrm{N}}/195 + \mathrm{PEC}_{\mathrm{C1\text{–}N}}/56.9 + \mathrm{PEC}_{\mathrm{C2\text{–}N}}/16.2 + \mathrm{PEC}_{\mathrm{C3\text{–}N}}/3.3$$

where $\mathrm{PEC}_{\mathrm{N}}$, $\mathrm{PEC}_{\mathrm{C1\text{–}N}}$, $\mathrm{PEC}_{\mathrm{C2\text{–}N}}$, and $\mathrm{PEC}_{\mathrm{C3\text{–}N}}$ are the estimated (based on mussel residue data) concentrations of naphthalene, C_1-naphthalenes, C_2-naphthalenes, and C_3-naphthalenes, respectively in the water at the station. The HI for total PAH is the sum of the HIs for the PAH fractions.

HIs estimated in this way for total PAH range from 0.00006 to 0.013 (Table 6). These values are lower by a factor of up to 5 than the HIs for total target hydrocarbons (Table 3). For example, the two stations with the highest estimated dissolved hydrocarbon concentrations, Ekofisk Station S4 and Tampen Station S5, have HIs of 0.033 and 0.045, and 0.010 and 0.013, respectively, when calculated based on total target hydrocarbons and the

Table 6
Hazard indices (HI) for the polycyclic aromatic hydrocarbon (PAH) fractions used in the dose-related risk and effect assessment model (DREAM) and total PAHs, based on estimates of aqueous concentrations of the fractions from mussel (*Mytilus edulis)* data (predicted environmental concentrations: PEC) and predicted no effects concentrations (PNEC) values (chronic toxicity) for all components in Table 5

Field/station	Naphthalenes	2/3-Ring PAH	4/5-Ring PAH	Total PAH
Tampen				
ST1	0.00037	0.00556	0.00022	0.00616
ST2	0.00058	0.00707	0.00026	0.00792
ST3	0.00038	0.00025	0.00000	0.00063
ST5	0.00249	0.01019	0.00040	0.01308
ST6	0.00009	0.00272	0.00009	0.00290
ST7	0.00005	0.00008	0.00000	0.00013
ST8	0.00004	0.00002	0.00000	0.00006
ST9	0.00016	0.00009	0.00000	0.00025
ST10	0.00011	0.00006	0.00000	0.00018
Ekofisk				
S1	0.00149	0.00513	0.00025	0.00687
S3	0.00005	0.00018	0.00004	0.00027
S4	0.00200	0.00771	0.00037	0.01009
S6	0.00062	0.00147	0.00007	0.00216
S7	0.00021	0.00035	0.00003	0.00059
S8	0.00009	0.00015	0.00003	0.00027
S9	0.00017	0.00048	0.00004	0.00069
S10	0.00011	0.00032	0.00004	0.00047
S11	0.00010	0.00048	0.00004	0.00062
S12	0.00007	0.00019	0.00004	0.00030
S13	0.00012	0.00049	0.00006	0.00067
R2	0.00009	0.00028	0.00007	0.00044

DREAM PAH fractions, respectively. The difference is due to the inclusion of more hydrocarbons, particularly the alkyl decalins and heterocyclics, in the HI based on all the measured hydrocarbons. Both approaches rank the stations in the same order. They also identify the 3-ring PAH as the greatest contributors to the potential toxicity of the surface waters in the Ekofisk and Tampen areas, particularly if the PNECs for decalins are overestimates, as discussed above.

3.3. Environmental risk assessment with DREAM model

DREAM estimated the concentration of PAH fractions, plus total target 2–5-ring PAH in surface waters at each sampling station in the Ekofisk and Tampen Regions (Table 7). Concentrations of total PAH estimated by DREAM were quite similar to concentrations estimated from mussel tissue residues for the Ekofisk stations, but not the Tampen stations. At stations in the Tampen Region where total PAH concentrations were above background, concentrations estimated by DREAM were 2–10 times higher than those estimated from the mussel residue data. The difference was greatest for the 2 stations within 0.5 km of a discharge. Mussels near the platform discharges are exposed to the most variable concentrations of produced water chemicals because of the meandering of the produced water plume due to the elliptical course of tidal currents during the diurnal tidal cycle. Thus, the "average" surface water concentration at stations near the discharges

Table 7
Comparison of predicted environmental concentrations (PECs) for the 3 polycyclic aromatic hydrocarbon (PAH) classes and total 2-5 ring PAHs in surface waters at selected sampling stations in the Ekofisk and Tampen Regions of the North Sea estimated from mussel (*Mytilus edulis*) tissue residue monitoring data and the dose-related risk and effect assessment model (DREAM)

Region/station	Naphthalenes		2–3 Ring PAHs		4–5 Ring PAHs		Total PAHs	
	Mussel	DREAM	Mussel	DREAM	Mussel	DREAM	Mussel	DREAM
Tampen								
ST1	13.5	5.0	6.00	0.5	0.37	0.05	19.8	5.55
ST2	18.6	168	7.66	27.4	0.46	0.57	26.8	196
ST3	16.1	22.1	1.48	4.26	<0.04	0.17	17.6	26.5
ST5	35.0	311	14.4	32.7	0.56	0.57	49.9	344
ST6	6.85	5.37	1.96	0.90	0.16	0.07	8.97	6.35
ST7	6.41	5.01	0.73	0.63	<0.04	0.05	7.14	5.69
ST8	5.33	5.0	0.27	0.5	<0.04	0.05	5.60	5.55
ST9	9.01	5.08	1.00	0.66	<0.04	0.05	10.0	5.80
ST10	7.00	5.0	0.58	1.02	<0.04	0.07	7.58	6.09
Ekofisk								
S1	17.7	20.1	9.27	2.10	0.32	0.07	27.3	22.3
S3	4.30	5.03	0.31	0.52	0.05	0.05	4.66	5.60
S4	22.5	29.6	13.8	2.60	0.46	0.07	36.8	32.3
S6	10.6	5.28	3.45	0.85	0.11	0.05	14.2	6.18
S7	6.63	5.66	1.02	0.54	0.04	0.05	7.69	6.25
S8	3.96	5.02	0.53	0.54	0.04	0.05	4.53	5.61
S9	5.48	5.61	0.98	0.67	0.06	0.05	6.52	6.33
S10	4.63	5.18	0.75	0.56	0.06	0.05	5.44	5.78
S11	4.00	5.35	0.99	0.62	0.05	0.05	5.04	6.02
S12	4.60	5.0	0.62	0.50	0.07	0.05	5.29	5.55
S13	5.31	5.0	1.44	0.50	0.07	0.05	6.82	5.55
R2	4.48	5.0	0.84	0.50	0.11	0.05	5.43	5.55

Concentrations are ng/L (parts per trillion).

estimated by DREAM may be significantly higher than the average exposure concentrations to mussels.

Output from DREAM normally includes a risk map showing the risk characterization ratio (RCR) for the modelled area, an EIF value giving the recipient water volume in which the RCR exceeds 1.0, and a pie chart showing the contribution to risk from the different groups of compounds in the discharge.

Individual RCRs, representing an index of environmental risk, of the PAH subgroups and total PAH in surface waters of the two regions range from 0.001 (essentially background risk) to 0.26 (Table 8). All RCRs determined by DREAM for both regions are below 1.0, meaning that no significant or unacceptable environmental risk of PAH was observed in the regions. The highest RCRs are predicted for the stations closest to the discharge points (0.5 km). The RCRs decline to background values at most sampling locations 10 km or more from the nearest discharge, in agreement with the measured and modelled PECs (Table 7). The RCR for surface water at Tampen Region Station ST3, located 10 km downcurrent from the nearest discharge, is 0.046, significantly higher than background, but is well below the 1.0 RCR value indicative of a possible ecological risk. The background RCRs are approximately 0.002, 0.003, 0.001 and 0.006 for naphthalenes, 2- and 3-ring PAH, 4- and 5-ring PAHs, and total PAH, respectively. At all stations, the

Table 8
Risk characteristic ratios (RCRs) for the 3 polycyclic aromatic hydrocarbon (PAH) fractions and total PAHs, estimated by dose-related risk and effect assessment model (DREAM)

Field/station	Naphthalenes	2-3 Ring PAH	4-5 Ring PAH	Total PAH
Tampen				
ST1	0.0024	0.0033	0.0010	0.0067
ST2	0.0799	0.1828	0.0115	0.2741
ST3	0.0105	0.0284	0.0033	0.0422
ST4	0.0025	0.0037	0.0010	0.0071
ST5	0.1481	0.2177	0.0115	0.3773
ST6	0.0026	0.0060	0.0015	0.0101
ST7	0.0024	0.0042	0.0011	0.0077
ST8	0.0024	0.0033	0.0010	0.0067
ST9	0.0024	0.0044	0.0010	0.0079
ST10	0.0024	0.0068	0.0015	0.0106
Ekofisk				
S1	0.0096	0.0140	0.0015	0.0251
S2	0.0026	0.0042	0.0010	0.0079
S3	0.0024	0.0035	0.0010	0.0069
S4	0.0141	0.0173	0.0015	0.0330
S5	0.0140	0.0168	0.0014	0.0322
S6	0.0025	0.0057	0.0010	0.0092
S7	0.0027	0.0036	0.0010	0.0073
S8	0.0024	0.0036	0.0010	0.0070
S9	0.0027	0.0044	0.0010	0.0082
S10	0.0025	0.0037	0.0010	0.0072
S11	0.0026	0.0042	0.0010	0.0077
S12	0.0024	0.0033	0.0010	0.0067
S13	0.0024	0.0033	0.0010	0.0067
R1	0.0024	0.0033	0.0010	0.0067
R2	0.0024	0.0033	0.0010	0.0067

RCRs are the DREAM generated risk values that are comparable to empirically generated hazard indices (HIs).

2- and 3-ring PAH group, including the naphthalenes, contribute most to the RCR. The high molecular weight 4- and 5-ring PAH contribute little to the estimated risk at all stations.

3.4. Comparison of environmental risk from DREAM and monitoring

RCRs derived from DREAM are higher than HIs derived from estimated concentrations in ambient water (based on mussel tissue residue data) for all 3 PAH groups and for total 2–5 ring PAH (Fig. 2). Differences in risk values are larger for the Tampen stations than for the Ekofisk stations. Differences in risk values estimated by the two methods are greater at stations near produced water discharges than at those distant from a discharge in both the Tampen and Ekofisk regions.

The RCR/HI ratios for the different PAH fractions at the most heavily contaminated stations range from 1.1 to 138 (Table 9). There are similar ratios for stations distant from produced water discharges where PAH concentrations often are at or near background levels. In most cases, RCR/HI ratios are higher at stations in the Tampen Region than at stations in the Ekofisk Region. Produced water discharge volumes are much higher in the Tampen Region than in the Ekofisk Region, probably resulting in much greater tidally

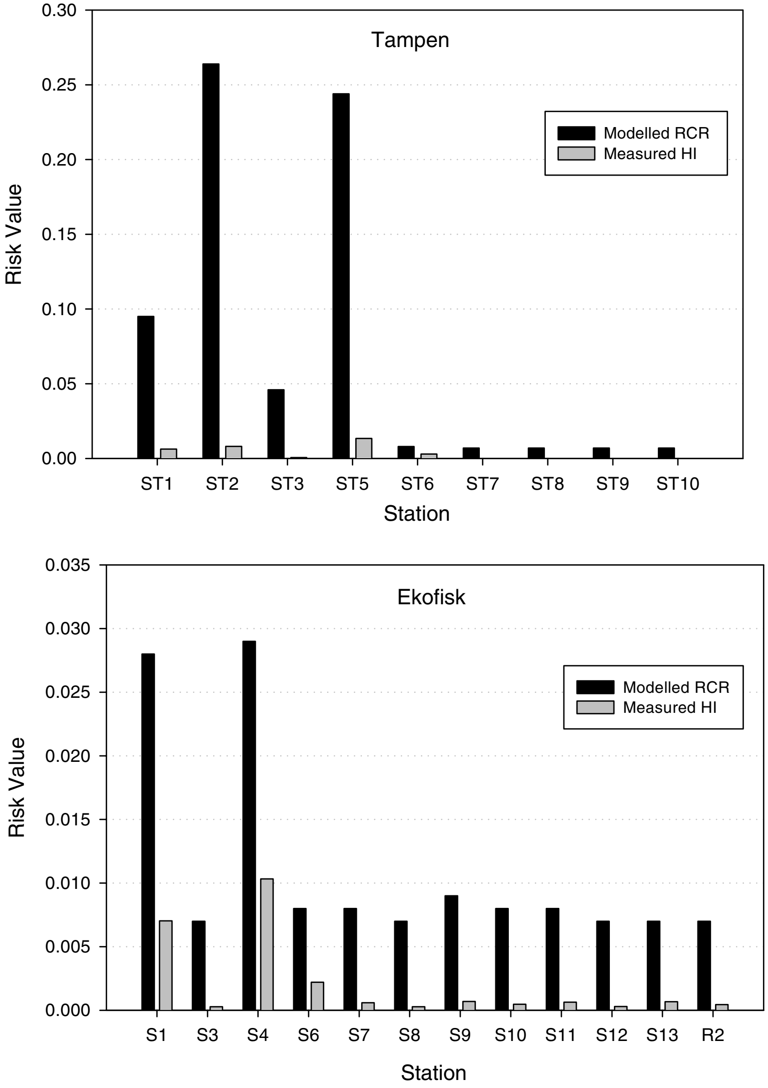

Fig. 2. Risk characterization ratios (RCRs) and hazard indices (HIs) for total polycyclic aromatic hydrocarbons (PAHs) at stations in the Tampen and Ekofisk Regions of the North Sea. RCR is the ratio of the predicted environmental concentration (PEC) estimated by the dose-related risk and effect assessment model (DREAM) to the predicted no effect concentration (PNEC) for selected hydrocarbon fractions. The HI is sum of the ratios of the measured PAH concentration in the water to a modelled PNEC value for each PAH analyte. A risk value of 1 or higher indicates a possible risk to the health of marine organisms from the site.

influenced variations in PAH concentrations in surface waters of the sampling stations. This is reflected in the greater differences between estimated (based on mussel residue data) and modeled PAH concentrations in surface waters near the Tampen discharges than in surface waters near the Ekofisk discharges (Table 7). In addition, hydrodynamic data used in the model are not concurrent with the period of mussel deployments; interannual

Table 9
Ratios of risk characteristic ratios (RCR; Table 8) to hazard indices (HI; Table 6) for 3 polycyclic aromatic hydrocarbon (PAH) fractions and total 2-5 ring PAHs for the most heavily contaminated surface waters in the Tampen and Ekofisk Regions

Region/station	Naphthalenes	2-3 Ring PAH	4-5 Ring PAH	Total PAH
Tampen				
ST1	6.4	0.6	4.5	1.1
ST2	138	25.9	44.1	34.6
ST3	27.7	114	NV[a]	67.0
ST5	59.5	21.4	28.7	28.8
Ekofisk				
S1	6.4	2.7	6.0	3.6
S4	7.1	2.2	4.2	3.3
S6	4.0	3.9	14.9	4.3
S7	12.8	10.3	33.3	12.4

[a] NV, no value. 4-5 ring PAHs were not detected in mussels (*Mytilus edulis*) from this location.

variations in local surface water current patterns could account for a large part of the difference between RCR and HI values.

The main cause of the differences between values for RCR and HI is in the PNEC values used to estimate these risk values. In DREAM, PNEC is estimated by dividing the lowest available chronic effects concentration by an assessment factor of 10–100 (Table 2), whereas the PNEC value in the HI calculation is estimated by dividing the geometric mean acute value by an acute/chronic ratio of 25. For example, concentrations of naphthalenes in water from Ekofisk Station S1, estimated from mussel data and the DREAM model, are nearly the same, 17.7 and 20.1 ng/L, respectively (Table 7). However, the RCR/HI ratio for naphthalenes at this station is 6.4 (Table 9). Four PNECs are required for estimating the HI for naphthalenes; they range from 195 μg/L for naphthalene to 3.34 μg/L for C_3-naphthalenes. The ambient measured concentration of these naphthalenes is divided by the respective PNEC to obtain a HQ. HQs for the four naphthalenes are summed to obtain the HI. The naphthalenes PNEC for the RCR estimation is 2.1 μg/L. The sum of the concentrations of naphthalene through C_3-naphthalenes, predicted by DREAM, is divided by this PNEC to obtain the RCR. Thus, the difference between RCR and HI in this case is due mainly to the difference in PNECs. Concentrations of all PAH fractions and total PAH, estimated by DREAM and from mussel data, are similar at nearly all the Ekofisk stations (Table 7), indicating that the RCR/HI ratios ranging between 2.2 and 33.3 are caused largely by the different PNEC values used.

There are large differences in concentrations of PAH fractions and total PAH, estimated by DREAM and from mussel data, in surface water samples from most of the Tampen Region stations less than about 5 km from the nearest produced water discharge (Table 7). The differences between estimated (based on mussel residue data) and modeled ambient concentrations (PEC) in surface waters at these stations combine with differences in PNECs to increase the RCR/HI ratios even further. For example, the largest RCR/HI ratio (174) is for naphthalenes in water from Tampen Region Station ST2, and estimated (based on mussel tissue residue data) and modeled total naphthalenes concentrations are 18.6 and 168 ng/L, respectively (Table 7). The higher modeled than estimated concentrations of PAH fractions in water near Tampen Region produced water discharges may be due to use of hydrodynamic and meteorological data for May 1990 instead of data for the period when mussels were deployed. As described earlier, physical oceanographic data were not available for the Tampen Region at the time of mussel deployment there in 1998; data for the same season (May) in 1990 were used. In addition, current speeds and directions are more variable and the water column is less well mixed in the Tampen Region than in the Ekofisk Region rendering estimates of mean concentrations in the water column more variable and less accurate.

4. Conclusions

In summary, the two methods for estimating ecological risk of PAH in produced water discharges to the Tampen and Ekofisk Regions of the North Sea give roughly comparable results. Both methods rank the different stations in a similar order and identify the 2- and 3-ring PAH fraction (represented by phenanthrene) as the most important contributor to the ecological risk of the PAH fraction of produced water. The DREAM model produces higher estimates of risk than the risk assessment based on field mussel monitoring data.

The difference in risk estimates is due primarily to differences in estimates of the chronic toxicity (PNEC) of the PAH fractions. The DREAM RCR is based on very conservative PNEC values. PNEC is derived from the lowest published acute or chronic toxicity value for a particular reference compound, to which an assessment factor of 10–100 is applied. Thus, the PNEC is an order of magnitude or more lower than the lowest observed effects concentration (the LOEC).

In the risk assessment based on field mussel monitoring data, the PNEC is based on a regression model relating acute toxicity to the log K_{ow} of the nonpolar organic contaminant. This relationship is based on the observation that most nonpolar organic chemicals behave as neutral narcotic agents and exert toxic effects when bioaccumulated to a critical body residue concentration (McCarty and Mackay, 1993). Estimated acute values are divided by a conservative acute/chronic ratio of 25 (Länge et al., 1998) to obtain the PNEC value. The chronic value obtained in this way can be considered an average or typical value, rather than a worst-case value. Di Toro et al. (2000) use the empirical relationship between acute toxicity and log K_{ow} as the basis for estimating the chronic toxicity of PAH to aquatic organisms. Their chronic values for naphthalene and phenanthrene are 320 μg/g and 32.4 μg/L, respectively. These PNECs are 2–3 times higher than PNECs used in the HI calculation and more than twenty times higher than the PNECs used in the DREAM model. The DREAM PNECs may be overly conservative. It is important that regulatory limits on chemical discharges be sufficiently conservative to fully protect the receiving water environment, but not so conservative that they require unnecessary energy and financial expenditures for compliance.

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