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# Monitoring of Polycyclic Aromatic Hydrocarbons (PAH) in Scottish Deepwater Environments (MoreDeep)

**Scottish Marine and Freshwater Science Vol 8 No 9**

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This report presents the results of marine and freshwater scientific work carried out by Marine Scotland Science.

# Monitoring of Polycyclic Aromatic Hydrocarbons (PAH) in Scottish Deepwater Environments (MoreDeep)

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## Executive Summary

Polycyclic aromatic hydrocarbon (PAHs) were measured in environmental samples (water, fish and sediment) collected in 2014 and 2016 from the Faroe-Shetland Channel and Rosemary Bank Seamount. These data could be used to provide a baseline against which any changes can be assessed in the event of an oil spill and contribute to any environmental impact assessment. Concentrations in all samples were low, often below the detection limits, and were typical of reference sites. Sponges can be used as an alternative indicator species to mussels for monitoring PAHs in the marine environment as they can accumulate PAHs from both the dissolved and particulate phase. PAH concentrations in marine sponges from Scottish waters have not previously been reported. Concentrations were low, but contained a higher proportion of heavier 4- to 6-ring PAHs compared to the fish samples.

## Introduction

Activities undertaken in Scottish deep waters, including fishing and oil exploration have the potential to impact on sensitive deep water ecosystems. Currently there is little baseline information on Scottish deep water ecosystems such as the Faroe-Shetland Channel (FSC), to the north west of the Shetland Isles, and the Rosemary Bank Seamount (RBS), to the north-west of the Outer Hebrides. Both areas have been proposed as marine protected areas (MPAs) for the protection of, among other features, deep-sea sponge aggregations. There is currently exploration and active extraction of hydrocarbons in the FSC whilst there is no such activity in the RBS. Should an oil spill occur, an Exclusion Zone will be enforced that can only be lifted once hydrocarbon concentrations are within background levels; therefore, it is crucially important to have background data of conditions prior to any spill.

Monitoring following an oil spill will require the analysis of environmental samples (sediment, invertebrates, fish and water) for hydrocarbons (*n*-alkanes, polycyclic

aromatic hydrocarbons (PAHs) and geochemical biomarkers and, where relevant, sensory assessment). Guidelines have been produced by the Centre for Environment, Fisheries and Aquaculture Science (CEFAS) as part of the PREMIAM (Pollution REsponse in Emergencies Marine Impact Assessment and Monitoring) project, as the official UK national approach to post-incident monitoring[1]. The background and information on the processes to be followed after an oil spill, including how to implement a monitoring programme and what to monitor, are covered in the PREMIAM guidelines.

Sensory assessment of fish and shellfish is one of the monitoring requirements following an oil spill. The use of a trained taste panel to assess petrogenic taint in fish and shellfish was used after oil spill incidents, such as the *Braer*[2] and Sea Empress. During these incidents sensory assessment was used as a component of the management of the fisheries closures. In the former case, taste-testing was used extensively; in the latter case, when PAH concentrations had returned to background, representative samples of fish or shellfish were taste-tested as a final proof that the fishery sector could be reopened. Marine Scotland Science (MSS) is the designated facility for sensory assessment of fish and shellfish within the UK National Contingency Plan for response to offshore incident.

While PAHs can occur naturally, the main environmental input is anthropogenic. PAHs can enter the environment as products of incomplete combustion of fossil fuels (pyrolytic) or from petrogenic sources. PAHs are constituents of crude oil and are present in the marine environment as a result of natural seeps, oil spills, shipping movements and from activities associated with offshore oil and gas exploration and production. PAHs are of concern as metabolites of some of the high molecular weight PAHs, such as benzo[*a*]pyrene, are potent animal and human carcinogens. In addition, the lighter 2-ring PAHs, which are the main PAH constituents of crude oil and some oil fractions, can result in the tainting of fish and shellfish[3]. This taint can be detected by a trained assessor. PAHs from pyrolytic sources comprise mainly of the heavier, parent (non-alkylated) PAHs.

Little baseline information is currently available for PAHs in the deep waters to the west of Scotland. Therefore, environmental samples (water, fish and sediment) were collected as part of a multidisciplinary survey in the FSC and from a control area on the RBS during September 2014 and 2016. All samples were analysed for PAHs, with the aim of providing baseline data which could contribute to any environmental impact assessment in the event of an oil spill. Sensory assessment was undertaken on the 2014 fish samples with the aim of widening the taste panels' experience of different fish species, in particular commercial deepwater species.

In addition, deep water sponges (*Geodia atlantica, Geodia barrette* and *Geodia phlegraei*) were collected for PAH analysis. MSS have no background data for PAH concentrations in sponges. In coastal areas blue mussels have been extensively used as sentinel indicator species for monitoring the uptake and accumulation of hydrophobic contaminants, such as PAHs, in the marine environment. PAHs can bio-accumulate in shellfish but are metabolised relatively effectively by fish. However, mussels are limited in their habitats and cannot indicate pollution levels at depth because they live in shallow coastal waters. Sponges are abundant benthic animals that are able to live in a wide range of habitats and can be found at depths of up to 7000 meters. In addition sponges can accumulate PAHs from both the dissolved and particulate phase; they have a high filtration rate, 1 kg of sponges can process over 24,000 L of seawater per hour, and can ingest particulates of 0.2-50 µm[4,5]. Previous studies have already demonstrated the efficacy of sponges to accumulate pollutants, therefore, they can be used as an alternative to mussels, and can in fact bio-accumulate PAHs to a greater extent than mussels[5-7].

This report presents the data from the PAH analysis of environmental samples (sediment, water, fish and sponges) and the sensory assessment of fish (2014 only) collected from FSC and RBS in 2014 and 2016.

## Experimental

### Sampling and Analytical Methods

Samples were collected from the Faroe-Shetland Channel (FSC) and from a control area on the Rosemary Bank Seamount (RBS) during September 2014 and again in September 2016 (Fig. 1) from the MRV *Scotia*.

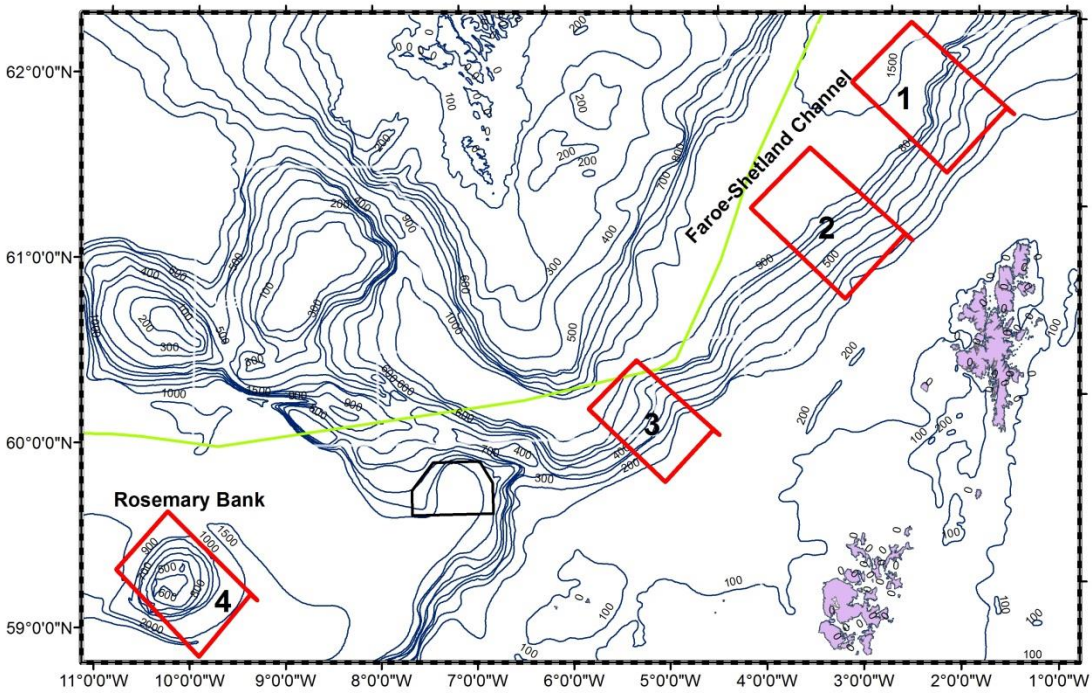
Water samples were collected from 1 and 10 metre depths at each site using a reverser bottle and transferred into pre-cleaned glass bottles (2.5 l). Samples were preserved by the addition of dichloromethane (100 ml) and kept at room temperature before extraction.

Fish were collected at each station using a bottom trawl. The species collected are shown in Table 1. In 2014 trawling was carried out at three locations along the FSC, Box 1-3, and at the control location, RBS (Figure 1). Five fish of each species were collected from each of the sites. Not all of the species were caught at each of the locations. These samples were stored at -20±5$^{o}$C prior to analysis. The fish were gutted and placed on ice for 24 hours prior to filleting. Fillets were wrapped in aluminium foil with one fillet from each fish blast frozen before all fillets were

transferred to the freezer and stored at - 20± 5 °C until required. The blast frozen fillet from each fish was for sensory assessment. Pools of five livers and five fillets were placed in solvent washed aluminium cans for hydrocarbon analysis. In addition, samples of sponges were collected using the bottom trawl from RBS in 2014. In 2016 fish and sponges were collected from RBS only, the FSC could not be sampled due to poor weather conditions. Fish species collected in 2016 included blue Ling (*Molva dypterygia*), black scabbard (*Aphanopus carbo*), blue whiting (Micromesistius poutassou) and round nose grenadier (*Coryphaenoides rupestris*).

Collecting sediment in deep water cannot be done using the normal Day Grab sampler as it takes too long for the grab to reach the seafloor. However, sediment samples were collected from the trawl doors in Box 1 and Box 2 in 2014 and from Rosemary Bank in 2016. The sediment was transferred to solvent washed aluminium cans and frozen (-20±5$^{o}$C) until required for analysis.

**Figure 1:** Environmental samples (water, fish, sediment and sponges) were collected at three locations along the Faroe-Shetland Channel (FSC, Box 1-3) and from a control area on the Rosemary Bank Seamount (RBS).




The species collected are listed with their abbreviations in Table 1.

## Table 1

Fish species collected for PAH analysis and sensory assessment in 2014 and 2016.

| Common Name | Latin Name | Abbreviation |
|---|---|---|
| Blue Whiting | *Micromesistius poutassou* | BWH |
| Greater Argentine | *Argentina silus* | GAR |
| Saithe | *Pollachius virens* | SAI |
| Blue Ling | *Molva dypterygia* | LIN |
| Greenland Halibut | *Reinhardtius hippoglossoides* | HAL |
| Megrim | *Lepidorhombus whiffiagonis* | MEG |
| Horse Mackerel | *Trachurus trachurus* | HMA |
| Black Scabbard | *Aphanopus carbo* Lowe | BSC |
| Roundnose Grenadier | *Coryphaenoides rupestris* | RNG |

### Sensory Assessment of Taint

A total of 38 individual fish were presented to the taste panel over four sessions for sensory assessment of hydrocarbon taint. The fish were cooked by microwave heating to a core temperature of 65°C and presented to the panel in lidded glass casseroles identified by a three digit random code. Assessors were asked to taste the fish and score any taint on a six point intensity scale (Table 2) recording the results on score sheets provided. Assessors were encouraged to comment on the texture and appearance of samples in addition to recording the presence or absence of taint. Taint can be defined as a taste or odour foreign to the product originating from external contamination. For the purpose of this investigation the panel were asked to assess samples for the presence of hydrocarbon taint, however, if any taint was observed, assessors were asked to describe the nature of the taint.

## Table 2

Taint intensity scale.

| Score | Interpretation |
|---|---|
| 0 | Absence |
| 1 | Slight |
| 2 | Moderate |
| 3 | Strong |
| 4 | Very strong |
| 5 | Extremely strong |

A sample is deemed tainted if more than half the panel scores (50%) are positive, regardless of the intensity of the taint recorded. If there are between 20% and 50% positive responses the sample is considered suspect for taint and untainted if the percentage positive scores are below 20%.

**Isolation of Hydrocarbons from Water**

Seven deuterated aromatic internal standards ($d_8$-naphthalene, $d_{10}$-biphenyl, $d_8$-dibenzothiophene, $d_{10}$-anthracene, $d_{10}$-pyrene, $d_{12}$-benzo[*a*]pyrene and $d_{14}$-dibenz[*a,h*]anthracene) were added to each water sample (2 l) before extraction with dichloromethane (2 x 100 ml). The extracts were combined and dried over sodium sulphate, solvent exchanged to *iso*-hexane and the extract reduced in volume by rotary evaporation prior to concentration to a small volume (~500 µl) under a nitrogen stream.

The aliphatic and aromatic hydrocarbons were separated by isocratic high performance liquid chromatography (HPLC). An aliquot (150 µl) of the *iso*-hexane extract was injected on to a previously calibrated Genesis SIL 4 µm HPLC column (25 x 4.6 cm id; Jones Chromatography, Mid Glamorgan, UK) and eluted with *iso*-hexane at a flow rate of 2 ml $min^{-1}$. The second fraction, (containing the aromatic hydrocarbons), was collected between approximately 2.5 and 20 minutes (split time accurately determined) and was stored at -20±5$^{o}$C for PAH analysis by gas chromatography-mass spectrometry (GC-MS).

**Isolation of Hydrocarbons from Fish (Flesh and Liver) and Sponges**

To a homogenised sample of fish muscle (~10 g from pools of five individual fish), fish liver (~1 g from pools of five individual fish) or sponges (~10 g) was added deuterated aromatic standards (d8-naphthalene, d10-biphenyl, d8-dibenzothiophene, d10-anthracene, d10-pyrene, d12-benzo[a]pyrene and d14-dibenz[a,h]anthracene). This was mixed with sodium hydroxide (10%, m/v) in methanol-water (9:1, v/v; 40 ml). The mixture was refluxed for 3 hours 45 minutes before the addition of water (10 ml). Refluxing was then continued for a further 15 minutes. The resulting hot solution was extracted with *iso*-hexane (2 x 80 ml). The combined extracts were washed with water (3 x 40 ml) before drying over sodium sulphate. The dried extract was concentrated to approximately 500 µl then fractionated by isocratic, normal phase HPLC (as described above), to separate the aliphatic and aromatic components prior to analysis by GC-MS.

**Isolation of Hydrocarbons from Sediment**

Each sediment sample was thoroughly mixed and an aliquot (approximately 10 g) removed for determination of water content by oven drying at 80 ± 5$^{o}$C for 22±2 hours. To a second aliquot of sediment (~ 20 g) was added the seven deuterated aromatic internal standards (d8-naphthalene, d10-biphenyl, d8-dibenzothiophene, d10-anthracene, d10-pyrene, d12-benzo[*a*]pyrene and d14-dibenz[*a,h*]anthracene). The hydrocarbons were extracted using dichloromethane/methanol with sonication. The halogenated solvent was isolated, dried over sodium sulphate and solvent exchanged to *iso*-hexane and the extract reduced in volume by rotary evaporation. The final extract was concentrated to a small volume (~500 µl) under a charcoal scrubbed nitrogen stream. The dried extract was then fractionated by isocratic, normal phase HPLC (as described above), to separate the aliphatic and aromatic components prior to analysis by GC-MS.

**Determination of PAHs in Sediment, and Fish Flesh and Liver by Gas Chromatography-mass Spectrometry (GC-MS)**

The concentration and composition of the PAHs (2- to 6-ring, parent and branched) were determined by GC-MS using an HP6890 Series gas chromatograph interfaced with an HP5973 MS and fitted with a cool on-column injector and a HP 5 MS column (30 m x 0.25 mm, 0.25 µm film thickness; Agilent, Stockport, UK). Helium was used as the carrier gas in constant flow mode (0.7 ml min$^{-1}$). Injections were made at 50$^{o}$C and the oven temperature held constant for three minutes. Thereafter, the temperature was raised at 20$^{o}$C min$^{-1}$ up to 100$^{o}$C. This was followed by a slower ramp of 4$^{o}$C min$^{-1}$ up to 270$^{o}$C, then at 40$^{o}$C min$^{-1}$ up to 290$^{o}$C, where it was held for three minutes, then at 40$^{o}$C min$^{-1}$ to a final temperature of 300$^{o}$C, where it was held for 22 minutes. The MS was set for selective ion monitoring (SIM) with a dwell time of 50 ms. Calibration standards, covering the concentration range 0.01 to 6.0 ng µl$^{-1}$ were analysed, in triplicate, and the average response used to compute the calibration curve. Correlation coefficients of at least 0.99 were achieved for all PAHs. Instrument limits of detection ranged from 0.05 to 0.2 µg kg$^{-1}$ for individual PAHs.

**Quality Control**

A procedural blank was analysed with the relevant batch of samples and final concentrations adjusted accordingly. Instrument suitability checks were run prior to analysing samples as a check on instrument performance. The analytical methods for the determination of PAHs in biota and sediment are accredited by the United

Kingdom Accreditation Services to ISO 17025. Internal quality control procedures include the incorporation of at least one laboratory reference material (LRM) in each batch of samples. The data from the LRMs were transferred to control charting software (NWA Quality Analyst) and Shewhart charts were produced with warning and action limits drawn at ± 2 x and ± 3 x the standard deviation of the mean. Quality assurance was further demonstrated through successful participation in the QUASIMEME (Quality Assurance of Information for Marine Environmental Monitoring in Europe) Laboratory Performance Studies.

## Results and Discussion

### Sensory Assessment

In total total nine different species (blue whiting, greater argentine, saithe, blue ling, Greenland halibut, megrim, horse mackerel, roundnose grenadier and black scabbard) were collected for sensory assessment in 2014. The sensory scores for each fish are detailed in Appendix 1. The panel size varied between 6 (session 3) and 14 (session 1) panel members. A total of 373 individual taint assessments were recorded, 11 returning a positive response. Two individual assessors were responsible for the positive scores. The panel leader contacted the assessors to investigate the responses and obtain more detail as to why their decisions had been made. Neither assessors were confident it was a hydrocarbon taint they had detected but felt some form of unusual flavour and odour was present.

### Polycyclic Aromatic Hydrocarbons in Fish (Liver and Flesh)

The liver and muscle tissue of pooled fish samples collected in 2014 and 2016 were analysed for PAHs. As expected, and consistent with the sensory assessment, PAH concentrations were low. Most PAHs were below the limit of detection (LoD) and with all PAHs being below the LoD in nineteen out of forty-eight fish muscle and liver samples. The highest total PAH (2- to 6-ring parent and alkylated) concentration was for a roundnose greanadier liver with a concentration of 45.9 µg $kg^{-1}$ wet weight. Where PAHs were detected they tended to be the lighter, more water soluble 2- to 3-ring PAHs.

Table 3 shows typical PAH concentrations in the muscle tissue of North Sea fish samples, alongside the PAH concentrations collected from RBS and FSC as part of this study. Following the *Braer* oil spill in January 1993, PAHs were measured in cod, haddock, plaice, whiting, lemon sole and dab from both within and out-with the Exclusion Zone. Total PAH concentrations in the reference fish muscle, collected

out-with the Exclusion Zone, ranged from 0.3 to 42.1 µg $kg^{-1}$ wet weight (Table 3)[2] Following the Captain (outer Moray Firth) oil spill in August 1997, PAHs were measured in haddock muscle and liver collected from out-with the Exclusion Zone and gave total PAH concentrations of 6.7 – 7.6 µg $kg^{-1}$ wet weight for muscle and 66.2 – 88.4 µg $kg^{-1}$ wet weight for liver (Table 2)[8]. Total PAH concentrations in reference plaice, lemon sole and witch from the Moray Firth ranged from 20.1 - 27.6 µg $kg^{-1}$ wet weight for the liver and from 1.9 – 7.9 µg $kg^{-1}$ wet weight in the muscle[8]. In 2002 muscle tissue from a range of commercial fish species (including haddock and flatfish), collected from the East Shetland basin and the Forties oilfields, were analysed for PAHs (unpublished data). There was no difference in PAH concentrations between fish collected in the near-field (< 5 km from an oil platform) and far-field (> 5 km from an oil platform) and mean total PAH concentrations were < 2 µg $kg^{-1}$ wet weight. Following a leak from a flow line to the Gannet Alpha platform during August 2011, fish samples were collected for hydrocarbon analysis to assess any environmental impact of the oil leak in the area. PAHs were measured in fish (lemon sole, whiting, plaice, cod and haddock) flesh. The highest total PAH concentration was 0.9 µg $kg^{-1}$ wet weight for a lemon sole[9]. Total PAH concentrations in the fish muscle collected from fish caught at six locations out-with the exclusion zone placed around the Elgin installation following a gas leak in 2012 ranged from 0.2 µg $kg^{-1}$ wet weight to 3.8 µg $kg^{-1}$ wet weight[10]. The total PAH concentrations in the pooled fish liver samples ranged from 5.4 µg $kg^{-1}$ wet weight to 57.4 µg $kg^{-1}$ wet weight. Total PAH concentrations found in the liver and muscle of fish sampled in 2014 and 2016 from RBS and FSC were within the ranges previously reported in fish.

## Table 3

Total PAH concentration (µg $kg^{-1}$ wet weight) ranges in different fish (muscle and liver) species.

| Species | Matrix | Area | Year | Range (µg $kg^{-1}$ wet weight) |
|---|---|---|---|---|
| cod | Muscle | North sea reference site | 1993 | 2.2 – 5.1[2] |
| haddock | Muscle | North sea reference site | 1993 | 0.8 – 11.2[2] |
| whiting | Muscle | North sea reference site | 1993 | 0.3 – 10.2[2] |
| lemon sole | Muscle | North sea reference site | 1993 | 2.4 – 13.0[2] |
| dab | Muscle | North sea reference site | 1993 | 4.9 – 42.1[2] |
| plaice | Muscle | North sea reference site | 1993 | 1.6 – 37.0[2] |
| Reference farmed salmon | Muscle | Shetland (outside Exclusion Zone following *Braer* oil spill) | 1993 | 3 – 60[2] |
| haddock | Muscle | Moray Firth reference site | 1997 | 6.7 – 7.6[8] |
| haddock | Liver | North Sea reference site | 1997 | 66.2 – 88.4[8] |
| flatfish | Muscle | Moray Firth reference site | 1997 | 1.9 – 7.9 |
| flatfish | Liver | North Sea reference site | 1997 | 20.1 – 27.6 |
| Commercial fish species, including haddock and flatfish | Muscle | East Shetland Basin, Forties Field | 2002 | Mean concentrations <2 |
| lemon sole, whiting, plaice, cod and haddock | Muscle | Gannet field (North Sea) | 2011 | <LoQ – 0.9[9] |
| lemon sole, plaice and haddock | Muscle | Elgin field (North Sea) | 2012 | 0.2 – 3.8[10] |
| lemon sole, plaice and haddock | Liver | Elgin field (North Sea) | 2012 | 5.4 – 57.4[10] |
| Various | Liver | Rosemary Bank (MoreDeep) | 2014 | < Lod – 4.74[10] |
| Various (Liver) | Liver | Faroe-Shetland Channel (MoreDeep) | 2014 | <LoD – 22.1 |
| Various (Liver) | Liver | Rosemary Bank (MoreDeep) | 2016 | <LoD – 45.9 |
| Various (Muscle) | Muscle | Rosemary Bank (MoreDeep) | 2014 | <LoD -0.93 |
| Various (Muscle) | Muscle | Faroe-Shetland Channel (MoreDeep) | 2014 | <LoD – 4.44 |
| Various (Muscle) | Muscle | Rosemary Bank (MoreDeep) | 2016 | <LoD – 0.76 |

### Polycyclic Aromatic Hydrocarbons in Sponges

Similar to the fish samples, PAH concentrations found in sponges collected from RBS were low; most PAHs were below detection limits and total PAH concentrations

ranged from 4.74 to 14.8 µg $kg^{-1}$ wet weight (28.71 to 54.09 µg $kg^{-1}$ dry weight). All samples had a higher proportion of the heavier (4- to 6-ring) parent PAHs (>40%), with fluoranthene, a 4-ring PAH, having the highest concentration in six out of the seven sponge samples, probably due to the sponges greater uptake from the particulate phase. This is in contrast to the fish where the lighter more water soluble 2- to 3-ring PAHs were detected more frequently than the heavier 4- to 6-ring PAHs. There are few published studies on PAH concentrations in marine sponges. Fluoranthene concentrations were reported as part of a study of marine sponges collected in Normandy in 2010 and gave a mean concentration of 209.2 µg $kg^{-1}$ dry weight[5]. The sponges showed a higher accumulation of fluoranthene compared to mussels. PAH concentrations were reported in sponges collected in a heavily polluted coastal area (Rio de Janerio), where total PAH concentrations (sum of 33 parent and branched 2- to 6-ring PAHs) ranged from 74 to 7,327 µg $kg^{-1}$ dry weight and with a higher proportion of the heavier 4 to 6-ring PAHs compared to mussels[6]. Although concentrations in RBS sponges were lower than these studies, they all showed a greater accumulation of the heavier PAHs.

**Polycyclic Aromatic Hydrocarbons in Water**

Water samples collected from each box at two depths (1 m and 10 m from the surface) were analysed for PAHs. Total PAH (2- to 6-ring parent and alkylated) concentrations in the water samples ranged from 4.3 ng $l^{-1}$ (FSC, 1 m) to 48.6 ng $l^{-1}$ (RBS, 10 m) (Table 4).

There is limited data available for PAH concentrations in Scottish offshore seawater, a summary of available data is given in Table 4. PAH concentrations were previously measured in water from a reference site at Loch Linnhe[11], and gave total PAH concentrations of between 27.8 and 33.1 ng $l^{-1}$. Following a leak from a flow line to the Gannet Alpha platform during August 2011, water samples were collected for hydrocarbon analysis to assess any environmental impact of the oil leak in the area[9]. Total PAH concentrations found in water samples were low, ranging from 9.9 to 34.1 ng $l^{-1}$. Concentrations found in water samples collected from the Stonehaven ecosystem monitoring site at two depths in April 2012 were 14.4 ng $l^{-1}$ in the 1 m sample and 7.9 ng $l^{-1}$ in the 10 m sample (unpublished data). In 2016, following a leak from the Clair platform, water samples were collected at five depths from ten sites, including a reference site, to assess any environmental impact of the oil leak in the area[12]. The total PAH concentrations in these water samples were low, ranging from 1.4 to 16.3 ng $l^{-1}$ and could be considered to be at background concentrations[12]. PAH concentrations in the water samples collected from the Faroe Shetland Channel and Rosemary Bank, were typical of previously reported background concentrations.

## Table 4

Total PAH concentration (ng $l^{-1}$ wet weight) ranges in water.

| Area | Year | Range (ng $l^{-1}$) |
|---|---|---|
| Loch Linnhe reference site | 2002 | 27.8, 33.1[9] |
| Gannet platform, North Sea | 2011 | 9.9- 34.1[7] |
| Stonehaven reference site | 2012 | 14.4 (1 meter)<br>7.9 (10 meter) |
| Clair field | 2016 | 1.6 – 14.7[10] |
| Rosemary Bank (MoreDeep) | 2014 | 20.6, 48.6 |
| Faroe-Shetland Channel (MoreDeep) | 2014 | 4.3 – 18.8 |
| Rosemary Bank (MoreDeep) | 2016 | 20.5, 22.4 |
| Faroe-Shetland Channel (MoreDeep) | 2016 | 14.8 – 24.7 |

### Polycyclic Aromatic Hydrocarbons in Sediment

Total PAH (2- to 6-ring parent and alkylated) concentrations in the sediment samples collected from the trawl doors in 2014 from FSC were 56.3 and 76.8 µg $kg^{-1}$ dry weight. In 2016 samples were collected from RBS only and concentrations ranged from 44.6 µg $kg^{-1}$ dry weight to 110 µg $kg^{-1}$ dry weight. Previous studies of PAHs in Scottish sediments classed total PAH (2- to 6-ring parent and alkylated) concentrations of < 150 µg $kg^{-1}$ dry weight as low, between 150 and 750 µg $kg^{-1}$ dry weight as medium and > 750 µg $kg^{-1}$ dry weight as high,[13] , therefore, the classification for PAHs in sediment from this study was low. PAH concentrations were normalised to 2.5% total organic carbon to compare to OSPAR background assessment concentrations (BACs) (Table 5). Naphthalene exceeded the BAC in two sediment samples, both collected from the RBS in 2016. All other PAHs were below the BACs, however, this was based on an individual point and didn't take into account the analytical variability. Effects Range Low (ER-L) values are used by OSPAR for the assessment of PAHs in sediment (Table 5). ER-Ls were developed by the United States Environmental Protection Agency for assessing the ecological significance of sediment concentrations. Concentrations below the ER-L rarely cause adverse effects in marine organisms. Concentrations for all PAHs were well below the ER-L.

**Table 5**

PAH concentrations (normalised to 2.5% organic carbon) in FSC and RBS sediment alongside OSPAR Background Assessment Concentrations (BACs) and Effects Range-Low (ER-Ls) for comparison.

| | **BAC* (µg $kg^{-1}$ dw) normalised to 2.5% TOC** | **ER-L (µg $kg^{-1}$ dw)** | **Concentration range in RBS and FSC sediment (µg $kg^{-1}$ dw) normalised to 2.5% TOC** |
|---|---|---|---|
| Naphthalene | 8 | 160 | 3.7 - 25.8 (mean = 9.6, SD = 7.7) |
| Phenanthrene | 32 | 240 | 14.1 – 31.3 (mean = 22.1, SD = 6.5) |
| Anthracene | 5 | 85 | 0.7 – 2.4 (mean = 1.1, SD = 0.9) |
| Fluoranthene | 39 | 600 | 3.3 – 6.3 (mean = 5.0, SD = 1.7) |
| Pyrene | 24 | 665 | 5.7 – 9.2 (mean = 8.1, SD = 1.2) |
| Benz[a]anthracene | 16 | 261 | 1.2 – 8.4 (mean = 3.3 SD = 2.9) |
| Chrysene (including triphenylene) | 20 | 384 | 7.3 – 17.0 (mean = 10.0, SD = 3.4) |
| Benzo[*a*]pyrene | 30 | 430 | 9.4 – 22.0 (mean = 13.3, SD = 3.4) |
| Benzo[*ghi*]perylene | 80 | | 9.2 – 26.8 (mean = 16.9, SD = 8.5) |
| Indeno[123-*cd*]pyrene | 103 | | 3.0 – 13.6 (mean = 8.2, SD = 6.3) |

The sources of PAH contamination can be identified by examining the PAH distribution and using PAH concentration ratios. PAHs of petrogenic origin will have a higher proportion of the lighter (2- and 3-ring), alkylated PAHs, whilst PAHs of pyrolytic origin have a higher proportion of the heavier (4- to 6-ring), parent PAHs. The proportion of parent PAHs was low (<40%) in both FSC and RBS sediments, ranging from 25 to 33.1%, which suggests a more petrogenic source of PAHs. There was a higher proportion of the 2- and 3-ring PAHs, again indicative of petrogenic sources of PAHs. The use of PAH concentration ratios for source identification has been reviewed (Table 6)[14]. The use of two or more ratios was recommended as environmental factors can influence the behaviour of individual PAH compounds. Using the diagnostic anthracene/(anthracene+phenanthrene) ratio (ANT/[ANT+PHEN]) and fluoranthene/(fluoranthene+pyrene) ratio (FLUT/(FLUT+PYR) the sediment PAHs in this study would appear to be primarily of petrogenic origin, with ratios less than 0.1 and 0.4, respectively.

The profile observed in the RBS and FSC sediment was different from previously observed in marine sediments. Pyrolytic PAHs are normally the dominant source of PAHs in the Scottish marine environment[15]. Sediments from Scottish locations (Shetland, Orkney and sea lochs on the west of Scotland, Fladen) have all shown

PAH profiles typical of a predominately pyrolytic source[15]. Atmospheric deposition of pyrolytic PAHs discharged from urban areas can result in widespread, low level PAH contamination at remote locations such as these[15]. The profile in the RBS and FSC indicates that atmospheric deposition of pyrolytic PAHs is less in these areas.

**Table 6**

PAH concentrations used to identify sources of PAHs[14].

| Ratio | Value | Source |
|---|---|---|
| Anthracene / (anthracene + phenanthrene) | <0.1 | Petrogenic |
| | >0.1 | Pyrolytic |
| Fluoranthene / (fluoranthene + pyrene) | <0.4 | Petrogenic |
| | 0.4-0.5 | Vehicle and crude oil combustion |
| | >0.5 | Coal / biomass combustion |

## Conclusions

1. Environmental samples were collected from the Faroe Shetland Channel and the Rosemary Bank Seamount in 2014 and 2016 to provide baseline PAH data for these areas to add to the existing Scottish baseline data to be used in any environmental impact assessment following an oil spill.

2. A range of commercial deep water fish were collected and sensory assessment and PAH analysis undertaken. The aim of the sensory assessment was to familiarise the taste panel with their taste and texture. All samples were deemed not to have any petrogenic taint. PAH concentrations were low in all species (flesh and muscle) and similar to data previously held for reference fish samples.

3. The PAH concentrations in water samples in both areas were low and also typical of background data.

4. PAHs were detected in three species of sponges, concentrations were low with many PAHs being below the detection limits. PAHs have not previously been reported in Scottish marine sponges. Similar to other published studies

the Scottish marine sponges showed a greater accumulation of the heavier 4- to 6-ring PAHs. Sponges may be useful as an indicator species for the analysis of PAHs in the marine environment, particularly in areas where other indicator species such as mussels cannot be found.

5. PAHs were measured in sediment samples collected from the trawl doors whilst sampling for fish in the RBS and FSC. Concentrations were low and would be classed as being at background for all PAHs except naphthalene. However, the PAH profile was different from other Scottish marine sediment, containing a lower proportion of PAHs of pyrolytic origin.

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## Appendix 1

Sensory assessment results of fish samples collected from the Faroe-Shetland Channel (Box 1-3) and Rosemary Bank Seamount in 2014.
NT, Not tainted

| Location | Species | LIMS ID | Sensory scores | Mean | % +ve | Taint |
|---|---|---|---|---|---|---|
| **Box 1** | BWH | Mar-2014-18549 | 0,0,0,0,0,0,0,0 | 0 | | NT |
| **Box 1** | BWH | Mar-2014-18550 | 0,0,0,0,0,0,0,0 ,0,0,0 | 0 | | NT |
| **Box 1** | GAR | Mar-2014-18554 | 0,1,0,0,0,0,0,0, 0,0,0,0,0,0, | 0.07 | 7.1 | NT |
| **Box 1** | GAR | Mar-2014-18558 | 0,0,0,0,0,0 | 0 | | NT |
| **Box 1** | SAI | Mar-2014-18559 | 0,0,0,0,0,0,0, 0,0,0,0 | 0 | | NT |
| **Box 1** | SAI | Mar-2014-18560 | 0,0,1,0,0,0,0, 0,0,0,0 | 0.09 | 9.1 | NT |
| **Box 1** | LIN | Mar-2014-18564 | 0,0,0,0,0,0,0,0 | 0 | | NT |
| **Box 1** | LIN | Mar-2014-18567 | 0,1,0,0,0,0,0,0, 0,0,0,0,0,0, | 0.07 | 7.1 | NT |
| **Box 1** | HAL | Mar-2014-18571 | 0,0,1,0,0,0,0,0,0,0, 0 | 0.09 | 9.1 | NT |
| **Box 1** | HAL | Mar-2014-18572 | 0,0,0,0,0,0 | 0 | | NT |
| **Box 2** | HAL | Mar-2014-18577 | 0,0,0,0,0,0,0,0,0,0, 0 | 0 | | NT |
| **Box 2** | HAL | Mar-2014-18578 | 0,0,0,0,0,0,0,0,0,0, 0 | 0 | | NT |
| **Box 2** | GAR | Mar-2014-18581 | 0,1,0,0,0,0,0,0, 0,0,0,0,0,0, | 0.07 | 7.1 | NT |
| **Box 2** | GAR | Mar-2014-18582 | 0,0,0,0,0,0 | 0 | | NT |
| **Box 2** | BWH | Mar-2014-18586 | 0,1,0,2,0,0,0,0,0,0, 0,0,0 | 0.21 | 14.3 | NT |
| **Box 2** | BWH | Mar-2014-18587 | 0,0,0,0,0,0,0,0 | 0 | | NT |
| **Box 2** | MEG | Mar-2014-18592 | 0,0,0,0,0,0,0,0 | 0 | | NT |
| **Box 2** | MEG | Mar-2014-18593 | 0,0,0,0,0,0,0,0 | 0 | | NT |
| **Box 2** | LIN | Mar-2014-18594 | 0,2,0,0,0,0,0,0, 0,0,0,0,0,0, | 0.14 | 14.3 | NT |
| **Box 2** | LIN | Mar-2014-18598 | 0,0,0,0,0,0,0,0 | 0 | | NT |
| **Box 3** | SAI | Mar-2014-18600 | 0,0,1,0,0,0,0,0,0,0, 0 | 0.09 | 9.1 | NT |
| **Box 3** | SAI | Mar-2014-18602 | 0,0,0,0,0,0,0,0 | 0 | | NT |
| **Box 3** | GAR | Mar-2014- | 0,1,0,3,0,0,0,0,0,0, | 0.29 | 14.3 | NT |

| | | | | | | |
|---|---|---|---|---|---|---|
| **Box 3** | **BWH** | **Mar-2014-18611** | **0,0,0,0,0,0,0,0** | **0** | | **NT** |
| **Box 3** | BWH | Mar-2014-18612 | 0,1,0,0,0,0,0,0, 0,0,0,0,0,0, | 0.07 | 7.1 | NT |
| **Box 3** | HMA | Mar-2014-18615 | 0,0,0,0,0,0,0,0,0,0 | 0 | | NT |
| **Box 3** | HMA | Mar-2014-18616 | 0,0,0,0,0,0,0,0,0,0 | 0 | | NT |
| **Box 3** | MEG | Mar-2014-18622 | 0,0,0,0,0,0 | 0 | | NT |
| **Box 3** | MEG | Mar-2014-18623 | 0,0,0,0,0,0,0,0 | 0 | | NT |
| **Box 3** | HAL | Mar-2014-18624 | 0,0,0,0,0,0,0,0,0,0 | 0 | | NT |
| **Box 3** | HAL | Mar-2014-18625 | 0,0,0,0,0,0 | 0 | | NT |
| **Rosemary Bank** | BSC | Mar-2014-18629 | 0,0,0,0,0,0 | 0 | | NT |
| **Rosemary Bank** | BSC | Mar-2014-18630 | 0,0,0,0,0,0 | 0 | | NT |
| **Rosemary Bank** | RNG | Mar-2014-18637 | 0,0,0,0,0,0,0,0 | 0 | | NT |
| **Rosemary Bank** | RNG | Mar-2014-18638 | 0,0,0,0,0,0,0,0 | 0 | | NT |
| **Rosemary Bank** | BWH | Mar-2014-18640 | 0,1,0,1,0,0,0,0,0,0, 0,0 | 0.14 | 14.3 | NT |
| **Rosemary Bank** | BWH | Mar-2014-18641 | 0,0,0,0,0,0,0,0,0,0 | 0 | | NT |
| | | 18604 | 0,0,0 | | | |
| **Box 3** | GAR | Mar-2014-18605 | 0,0,0,0,0,0 | 0 | | NT |