Environmental forensics evaluation of sources of sediment hydrocarbon contamination in Milford Haven Waterway.

Journal:	*Environmental Science: Processes & Impacts*
Manuscript ID:	EM-ART-10-2014-000522.R1
Article Type:	Paper
Date Submitted by the Author:	21-Nov-2014
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Environmental Impact Statement: Milford Haven Waterway

The detailed forensic analyses of 2010 data have identified PAHs from present-day refinery effluent and from historic sources: the *Sea Empress* HFO, and possibly from *El Omar* and WW2 tank-farm fires. Domination of fingerprints in the <2 cm sediments across the waterway by the historic pollution sources suggests disturbance of settled sediments, most likely by dredging. The forensic analyses help to facilitate a fuller and more technically defensible assessment of the ecological impact of the incidents (*e.g.* both *Sea Empress* and *El Omar*) and of major engineering works (*e.g.* LNG). The geochemical markers also effectively act as sediment tracers that substantiate sediment and contaminant transport patterns predicted previously for MHW using sediment trend analysis.

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Received (in XXX, XXX) Xth XXXXXXXXX 20XX, Accepted Xth XXXXXXXXX 20XX
DOI: 10.1039/b000000x

Abstract

Current and historic petroleum-related activities in Milford Haven Waterway (Wales, UK) contribute to hydrocarbon contamination of surficial sediments. Three main hydrocarbon components of sediments were analyzed: (1) Aliphatic hydrocarbons of predominantly biogenic origin, representing about 5-15% of total hydrocarbons (THC); (2) Polycyclic aromatic hydrocarbons (PAHs) from recent petrogenic and mainly older pyrogenic sources, representing about 2-6% of THC; (3) Unresolved complex mixture from spill-related and heavily-weathered petrogenic sources, representing as much as 70-85% of THC. Environmental forensics evaluation of the data demonstrate that although 72,000 tonnes (t) crude oil spilled from the *Sea Empress* in 1996, the Forties blend cargo was not identified in 2010. However, using biomarkers, heavy fuel oil from *Sea Empress'* bunkers (480 t spilled) was detected further upstream and more widely than previously. Iranian crude (100 t) spilled by the *El Omar* in 1988 and fuel (130,000 t) lost during bombing in 1940 also were tentatively identified. The PAH source ratios demonstrate that the historic pyrogenic PAHs come mainly from biomass and coal combustion. The distribution pattern of PAHs appeared more pyrogenic in 2012 than in 1996, as if recovering from the more petrogenic signature, in places, of the *Sea Empress*. The heavier PAH distributions were pyrogenic at most stations, and similar to those in sediments from oil terminal berths up to 2006, when dredging operations peaked. Partly as a result of this, in 2007 the concentrations of PAHs peaked throughout the waterway. Apart from atmospheric and runoff inputs, most of the identified inputs to the surficial sediments are historic. Therefore, likely processes include disturbance by construction and dredging of contaminants sequestered in sediments, followed by their wide redistribution *via* suspended sediment transport.

Introduction

Milford Haven Waterway (MHW) supports internationally-important habitats in a deep water ria-estuary in Wales representing one third of the UK's resource of this type of estuary (Figure 1). The port is the UK's third in terms of tonnage handled, with about 30% of the seaborne trade in oil and gas in 2012. MHW has a long history of receiving industrial and municipal pollution from chronic inputs and accidental releases. The inlet shows evidence of fine-grained sediment mobility affecting the fate and effects of oil and metal contaminants (Little[1-5], and McLaren[6]).

From 1960, with four oil refineries and associated marine jetties (currently only two), a terminal linked to a distant refinery, and an oil-fired Pembroke power station (all three now closed), petroleum inputs reached their highest level in the late 1960s to early 1970s. Liquefied natural gas (LNG)-related development operated by Dragon LNG and South Hook LNG has renewed industrial investment, coming on stream during 2008-09. In late 2012 RWE npower commissioned a new gas-fired power station. By 2010 the throughput of LNG in MHW exceeded 10.5 million t, about 50% of the total LNG handled by all UK ports.

Crude oil feedstocks from a variety of oil formations around the world, including the Middle East, West Africa, North Sea and Venezuela, have been processed by the local refineries during different periods of operation (*e.g.* Middle East dominant until 1978, North Sea from 1979, and North Sea with increasing West African crudes from 2000). The history of oil tanker spills in MHW began in 1960 with *Esso Portsmouth*, the first tanker to unload. There have since been many spills of varying size, mostly small, but some larger spills of light, non-persistent petroleum products (*e.g.* 2,300 t of gasoline from *Dona Marika,* 1973). The main tanker spills of crude oils were *Chryssi P. Goulandris* (1967), *El Omar* (1988) and *Sea Empress* (1996).

The largest oil spill occurred as a result of the grounding of the *Sea Empress* in the entrance of MHW on 15 February 1996. Over the following week, approximately 72,000 t of Forties blend crude oil and 480 t of heavy fuel oil (HFO bunkers) were lost. Because initially most of the crude oil and some 250 t of fuel oil were released on ebbing tides and in northerly winds, and also because of the use of chemical dispersants, the majority of oil was carried offshore and diluted into deeper water. However, the oil affected 200 km of Pembrokeshire shoreline mostly outside of the estuary mouth (Little[7], and SEEEC[8]). Further spills of HFO occurred on 21 February, when during the transfer of bunkers from *Sea Empress* at the Herbrandston (now South Hook LNG) jetty, 230 t leaked from a damaged internal pipe (SEEEC[8], and Harris[9]). As a result, the cargo was mainly physically and chemically-dispersed, and the HFO mainly affected the lower and middle reaches of MHW.

Following the *Braer* (1993, in Scotland) and the *Sea Empress* incidents a concerted effort was made to formalise UK sampling and analytical methods (Faksness[10], and Environment Agency[11]). Regulators and other stakeholders (*e.g.* the International Tanker Owners Pollution Federation; ITOPF) are satisfied by the modified Nordtest method in terms of identifying spilled oils. Sophisticated forensic levels of analysis are not needed for each and every sample taken during a spill or indeed for every spill where the source is small and well-known by all concerned. In the period between 2001 and 2008, MHW had almost 200 recorded very minor oil spills, but involving only 8.14 t oil lost in total. This was one of the more quiescent periods in the history of the port, for example in 1999 and 2000 there was about 10 t spilled in less than 20 incidents in each year (Little[4]). Nevertheless, forensics are too often perceived as largely unnecessary, or too expensive, in many UK spill and effluent impact studies except for the short-term application of establishing the initial identity of the spiller. The problem is that this source identification becomes more difficult in industrialized areas over time. The objective of this study is to differentiate among the multiple potential sources of hydrocarbon contamination in fine-grained surficial sediment (<2 cm deep) within accretional areas of MHW.

Materials and Methods

A hydrocarbon fingerprinting analysis was performed for 16 stations on the 2010 sample data obtained by the Milford Haven Waterway Environmental Surveillance Group (MHWESG) using the analytical laboratory ERT (ERT[12]). MHWESG and ERT also supplied 18 reference samples of oil or effluent. In order to compare to the 2010 data, forensic analyses were then conducted on surface sediments collected by the same field sampling personnel at the same stations by Countryside Council for Wales (CCW) in 2007 and 2012. In fact, all the MHW area-wide samples since 1993 and considered in this article were taken at the same time of year (October-November). The sample data obtained before and after 2010 were commissioned from the National Laboratory Service (NLS) by CCW for their monitoring of compliance with the European Union (EU) Habitats Directive. Note that in April 2013 Natural Resources Wales assumed the functions of CCW and Environment Agency (EA, Wales), among others. Also, in August 2010, Fugro Geosciences acquired ERT Scotland, but the earlier names in both these cases are used throughout this article.

Figure 1 shows the sampling station locations. Table 1 lists the sediment and reference oil source samples analyzed, with station identifications and locations (see Table 1 footnotes for sample dates and further details).

ERT employed a sample preparation procedure consistent with those used in previous investigations: soxhlet extraction of sediments with methanol, followed by extraction with dichloromethane (DCM). Methanol extracts were then re-extracted with pentane and combined with DCM extracts for the clean-up with silica gel. The NLS laboratory followed a newer procedure using an Accelerated Solvent Extraction (ASE) system with 50/50 DCM/acetone solvent mixture, followed by silica gel clean-up.

ERT participates in inter-laboratory performance evaluation studies for polycyclic aromatic hydrocarbons (PAHs) in marine sediments (*Quasimeme* Code MS-3). ERT's standard hydrocarbon methods are approved for ISO 17025:2005. Their detection limits for US EPA 16 PAH are 0.1 µg/kg per compound, and for 2-6 ring alkyl PAH are 1 µg/kg per group, both on a sediment dry mass basis.

NLS uses Measurement Reporting Verification (MRV), also participates in *Quasimeme*, and with the exceptions of the PAH alkyl homologues and tributyl tin (TBT), their methods are UKAS-accredited. NLS state that all the QA/QC criteria were met, including the MRVs of 0.5 µg/kg PAHs (note that for Benz[*a*]anthracene, the MRV is 5 µg/kg). The detection limits for other contaminants analysed by NLS are Cd 0.01 µg/kg, Hg 0.001 µg/kg, Cr 0.05 µg/kg, Cu 0.1 µg/kg, Pb and Zn 0.2 µg/kg, and polychlorinated biphenyls 0.1 µg/kg.

Both ERT and NLS analyze a certified reference material (CRM) standard with every sample batch. Reported precision is typically better than 15% for PAHs and 10% for metals, very similar to earlier studies on hydrocarbons and metals in MHW (Little[1, 3, 4]).

To evaluate the potential hydrocarbon sources, analytical data for 2010 was divided into three main categories: (1) aliphatic hydrocarbon concentrations obtained using gas chromatography with flame ionization detection (GC/FID); (2) polycyclic aromatic hydrocarbon (PAH) concentrations obtained using gas chromatography-mass spectrometry (GC/MS); and (3) petroleum biomarker (steranes and terpanes) distribution patterns also obtained by the GC/MS method.

Results

We present the analysis of each of the above three categories of data to evaluate their hydrocarbon fingerprinting value for differentiating among the potential sources of hydrocarbon contamination in surface sediments in the estuary. Table 2 shows the PAH 2010 data and Table 3 shows selected ratios for reference samples in 2010 (ERT[12]). Table 4 shows analytical data for total PAHs and heavy metals generated by NLS for 2007 and 2012.

Aliphatic hydrocarbon fingerprinting data

The GC/FID data evaluation is focused on the boiling range and distribution pattern of normal alkanes (n-alkanes) and selected iso-alkanes (such as pristane and phytane), which are the most abundant and easily identified compounds in non-weathered hydrocarbon samples. The analysis also ascertains the boiling range and shape of the unresolved complex mixture (UCM), observed as a baseline rise over a broad retention-time window of the gas chromatogram. As an example, the gas chromatogram of a Forties crude oil reference sample is shown in Figure 2.

Because n-alkanes are among the hydrocarbons that are most susceptible to biodegradation, their concentrations and distribution patterns change as a result of exposure to weathering in the aquatic environment. As oil degrades, the resolved compounds are removed and the UCM shifts toward the higher molecular weight constituents that are more resistant to degradation. The changes observed can often be used to evaluate weathering of crude oil or petroleum product due to environmental exposure (Hunt[14], Kaplan[15], and Wang[16]).

Gas chromatograms of surficial sediment samples (ERT[12]) exhibited a broad UCM signal spanning a range from approximately n-C_{16} (n-hexadecane) to n-C_{36} (n-hexatriacontane), with a suite of resolved peaks superimposed over the UCM (see example in Figure 3 for Sample CPL). The dominance of UCM is indicative of a relatively high degree of petroleum weathering and suggests that old pollution events are the most likely sources of the hydrocarbon contamination. Peaks corresponding to n-alkanes lighter than n-C_{20} are hardly detectable. Together with a very low content of iso-alkane phytane, this argues against large contributions from recent petroleum releases.

All the sediment sample chromatograms exhibit discernible n-alkane peaks in the n-C_{21} to n-C_{35} range with a predominance of odd-carbon-number alkanes, typical of mainly biogenic sources, such as leaf waxes of higher plants (Eglinton[17]). These GC/FID results indicate that both anthropogenic contamination and natural sources have contributed to hydrocarbon composition of the MHW sediments.

Due to the apparent matrix interference with n-C_{17} and pristane peaks in the sample chromatograms (see note to Figure 3), a traditional fingerprinting parameter (Pr/Ph ratio) could not be applied for a more detailed differentiation between the potential sources of petroleum-related aliphatic hydrocarbons. The potential utility of the Pr/Ph ratio can be perceived based on the broad range of its values among the reference oil samples analyzed: from Pr/Ph = 0.5 in Venezuelan crude to 2.6 in Nigerian (Agbami) crude (ERT[12]).

Sources of PAH contamination

Distribution patterns of individual PAHs. Because it is situated in a moderately densely-populated and industrialized area, MHW is subject to chemical contamination from a variety of sources and *via* many pathways. One ubiquitous category of pollutants is PAHs, and these are also of interest in monitoring the fate and effects of petroleum due to their aquatic toxicity, persistence, and in some cases carcinogenicity. There are numerous sources of PAH ranging from anthropogenic to natural environmental sources, all of which increase the complexity of the hydrocarbon contamination source analysis. Both unburned and burned fossil fuels impart their PAH signature to sediments in the marine environment. Simoneit[18] showed that PAH can originate from a variety of anthropogenic sources in both rural and urban areas by thermal combustion processes (*e.g.* coal burning, heating oils, and cooking), vehicular emissions (*e.g.* automobiles, trucks, locomotives and ships), and biomass burning (*e.g.* fireplaces, grassland, moorland and forest fires, and formerly, controlled farmland burning). All the common PAH sources identified above, as well as the site-specific sources related to refinery activities were previously identified as potential causes of sediment contamination in the study area (Little[4]).

General origins (petroleum- or combustion-related) of PAH contaminants are typically identified by evaluation of distribution patterns of individual hydrocarbons and selected parameters (Kaplan[15], Wang[16]). Analysis of the MHW sediments sampled in 2010 revealed the presence of a full suite of 2-, 3-, 4-, 5- and 6-ring PAH compounds (Table 2) with very similar distribution patterns in all the samples analyzed (ERT[12]). Representative PAH distribution characteristics observed in the study area are shown in Figure 4 for Sample MH4 off the former mine depot jetty at Newton Noyes near Milford Haven. The distribution exhibits an elevated content of heavier, 4-, 5- and 6-ring PAH compounds and descending distribution patterns of fluoranthene/pyrene and chrysene homologous series, C_0-PAH > C_1-PAH > C_2-PAH > C_3-PAH > C_4-PAH. Both of these characteristics are typical of pyrogenic sources. At the same time, the sample also contains relatively high concentrations of 2- and 3-ring PAH compounds with a typical petrogenic "bell-shaped" homologous series profile, C_0-PAH < C_1-PAH < C_2-PAH > C_3-PAH > C_4-PAH. The widespread abundance of these petrogenic PAH compounds and their moderately-weathered signature suggests a relatively recent and ubiquitous source. The observed combination of distribution patterns suggests that both pyrogenic and petrogenic sources have contributed to the PAH contamination of MHW sediments.

Pyrogenic PAH source ratio analysis. A source ratio-based approach was employed in this study to further differentiate among the potential sources of pyrogenic PAH contamination in the MHW sediments. According to Yunker[19], Oros[20] and Costa[21], the most common diagnostic ratios for the identification of pyrogenic sources are:

1 Anthracene/(Anthracene + Phenanthrene) [AN/(AN+P)]
2 Fluoranthene/(Fluoranthene + Pyrene) [FL/(FL+PY)]
3 Benz[*a*]anthracene/(Benz[*a*]anthracene + Chrysene) [BA/(BA+C)]
4 Indeno(1,2,3-*cd*)pyrene/(Indeno[1,2,3-*cd*]pyrene + Benzo[*ghi*]perylene) [IN/(IN+BPE)].

Using these ratios, it is often possible to differentiate among major sources of combustion-derived PAH such as fossil fuel and biomass. Based on the PAH source ratio measurements compiled by Yunker[19], the AN/(AN+P) ratio <0.10 indicates dominance of petroleum and >0.10 indicates dominance of combustion sources; the FL/(FL+ PY) ratio <0.40 indicates petroleum, 0.40–0.50 indicates petroleum combustion, and >0.50 indicates combustion of coal, grass/stubbles and wood; the BA/(BA+C) ratio <0.20 indicates petroleum, 0.20–0.35 indicates petroleum combustion, and >0.35 indicates combustion; and the IN/(IN + BPE) ratio <0.20 indicates petroleum, 0.20–0.50 indicates petroleum combustion, and >0.50 indicates combustion of coal, grasses and wood.

To compare PAH source ratios calculated for the sediment samples from the MHW to the source-specific values listed above, the ratios AN/(AN+P), BA/(BA+C), and IN/(IN + BPE) were plotted against the FL/(FL+ PY) ratio. The resulting cross-plots showing how MHW sediment samples distribute against possible PAH sources are presented in Figure 5.

The evaluation of the cross-plots in Figure 5 demonstrates that based on the source-ratio parameters, higher molecular weight pyrogenic PAH compounds in the surficial sediment samples of MHW predominantly originate from biomass and coal combustion. It should be noted that hydrocarbon accumulation from coal over longer timescales than the post-1960 oil industry, is suggested by radionuclide dated core studies of mudflats near Hook colliery in the inner MHW, which bisects the Pembrokeshire coalfield. Hydrocarbon and metal concentrations had been declining through the 1930s as the coal industry declined (Little[2]). Unfortunately, no required analytical data for the reference sample of colliery anthracite were made available for this study.

Petrogenic PAH source ratio analysis. PAH diagnostic ratios are also commonly used to differentiate petrogenic sources in moderately weathered environmental samples. Their application is based on the finding that biodegradation of certain alkylated PAH exhibits nearly identical first-order rate constants and, therefore, the concentration ratios of these compounds retain the initial oil signature. These ratios are termed "source" ratios, in contrast to ratios that change substantially with degradation and thus are termed "weathering" ratios. Ratios of C3-dibenzothiophenes/C3-phenanthrenes (C3D/C3P) and C2-dibenzothiophenes/C2-phenanthrenes (C2D/C2P) are known to be the most stable petroleum source ratios (Douglas[22]).

The petrogenic PAH source ratio evaluation is shown in Figure 6 (see Table 3 for source ratios of the reference samples). This double-ratio plot demonstrates that sediment samples (except ECL) cluster around the reference sample Refinery Waste Water Treatment Plant (RWWTP) Final Effluent. In spite of major improvements in effluent quality over time (Little[4]), based on these diagnostic source ratios, the refinery-related final effluent still appears sufficiently oily to contribute area-wide to relatively recent PAH contamination in the MHW surficial sediment samples.

Characteristically, the treatment plant effluent source-ratio parameters appear to reflect contributions from a mixture of different feedstocks, rather than a single reference crude oil. An elongated shape of the cluster in Figure 6 also suggests that petrogenic PAH contamination of sediments may have a significant contribution from Africa-sourced crude oils, as typified by the reference samples of Bonny crude oil and to a lesser extent Agbami and Amna crude oils. Recent petrogenic PAH contributions from Nigerian and Libyan crude oils appear to be consistent with the steadily increasing volumes of African crude oil feedstock being processed at local refineries as production in the North Sea declines (*Downstream*[23]).

Biomarker fingerprints for UCM source identification

Evaluation of the analytical data provided by MHWESG (ERT[12]) demonstrates that target alkanes constitute 5-15% and target PAH compounds constitute 2 - 6% of the total hydrocarbon concentration (THC). Most of the hydrocarbon content in the MHW surficial sediment is represented by the unresolved complex mixture (UCM is 70 - 85% of THC), indicating that the dominant portion of contamination is heavily weathered and originates from historic petroleum-related sources. Considering that the refinery effluent PAH distribution suggests rather fresh oil and that its total contribution is no more than 1-2% of THC, there is not likely to be much current effluent contribution to UCM.

The UCM often dominates solvent extracts from estuarine and coastal sediments near industrial areas. Despite speculation that biogenic sources also contribute to the UCM it has been shown recently by White[24] that UCM and separate saturate and aromatic fractions thereof are predominantly (>90%) fossil-derived. Even the polar fraction of the UCM is in fact composed of 66% fossil carbon indicating the presence of petroleum residues that have been transformed into more polar derivatives.

Fingerprinting of such petrogenic sources as those comprising the UCM is commonly performed based on petroleum biomarkers, mainly terpanes and steranes. Biomarkers in this context are complex organic molecules derived from formerly living organisms. The biomarkers found in crude oils are stable and show little or no changes in structures from their biogenic precursors in living organisms, and thus carry information about the nature, source formation, type, geological conditions, and thermal history of crude oil generation and maturation. Relative to other hydrocarbon groups such as alkanes and most aromatic compounds, biomarkers are more degradation-resistant, which makes them particularly useful tools for source identification of petroleum-derived contaminants in aquatic environments (Hunt[14], Kaplan[15] and Wang[16]).

Although terpanes and steranes are among the most recalcitrant components of crude oil, depending on the site-specific conditions some of them can be degraded to a certain degree after prolonged exposure in the aquatic environment. That is why not all biomarkers retain their power to resolve contaminant sources for the fingerprinting of older, severely weathered hydrocarbon contamination. Typically the most stable biomarkers include triaromatic steranes and the terpanes such as 17α(H),21β(H)-hopane (30ab), 17α(H),21β(H)-30-norhopane (29ab), 18α(H)-22,29,30-trisnorhopane (27Ts) and 17α(H)-22,29,30-trisnorhopane (27Tm). Several ratios among these biomarkers (ERT[12]) are evaluated in this study for further differentiation between the potential sources of heavily weathered historic petroleum-related contamination in the MHW surficial sediment (see Table 3 for selected source ratios of the reference samples).

The results of the contaminant source evaluation based on biomarker ratios are shown in Figure 7. The cross-plot utilizing 29ab/30ab and 27Ts/27Tm ratios demonstrates, perhaps surprisingly, that the biomarker diagnostic source ratios of all the MHW surficial sediment samples are noticeably different from those for *Sea Empress* Forties blend cargo and Forties crude, or indeed most other North Sea, Middle Eastern, Venezuelan and African reference crude oils that typify feedstocks supplied to the refineries in Milford Haven. Instead, all the biomarker source ratios for sediment samples cluster together with those for reference samples of *Sea Empress* HFO (SE Bunker), as well as Iranian crude oil and RFA *Darkdale* (but not HMS *Royal Oak*) fuel oil reference samples (Figure 7). On the basis of the terpane double ratios, *Sea Empress* HFO appears to have spread to all stations in MHW.

Further evaluation of the biomarker data available revealed that *Sea Empress* HFO (SE Bunker) and Iranian crude oil reference samples exhibit noticeably different distribution patterns of steranes. The observed differences provided another means for differentiation of the hydrocarbon sources in the MHW sediment.

As shown in Figure 8, a cross-plot of terpane source-ratio 29ab/30ab and triaromatic sterane source-ratio C20TA/C21TA has separated the sediment samples into two clusters: (**A**) - containing samples from the main estuarine channel and the low- and mid-section bays and tributaries (*e.g.* Angle Bay, Pembroke River and Cosheston Pill), and (**B**) - containing samples from the uppermost reaches and sub-estuaries of MHW (*e.g.* Western and Eastern Cleddau rivers, Cresswell and Carew rivers). Cluster (**A**) also includes reference samples of *Sea Empress* HFO (SE Bunker), whereas cluster (**B**) contains reference samples of Iranian heavy crude oil. In this cross plot, both RFA *Darkdale* and Iranian light crude fall away from the single cluster they had occupied in Figure 7 together with all the marine sediments (Figure 8).

Discussion

We shall consider the extent to which the observed spatial distribution of the hydrocarbon source-relationships among the 2010 surficial sediment samples in MHW is consistent with the well-documented extent of shoreline oiling following the *Sea Empress* oil spill in 1996. The sediment samples included in Figure 8 cluster (**A**) were collected in 2010 from areas that had been visibly oil-contaminated shorelines in late February 1996. Comparisons with field observations and historic hydrocarbon data were made from the literature for MHW and the authors' unpublished field notes and videotapes. Although oil sheen was observed on surface waters in the lower Western and Eastern Cleddau, and a few patches of darker oil on water were tentatively identified as far as Llangwm in the first few days, significant whole oil visibly penetrated MHW only as far as the Cleddau road bridge (MPCU[25], Arthur D. Little[26] and Little[7]). About 400 t of chemical dispersants were sprayed during the ebb tide on the Forties crude oil outside the estuary, and it is possible the dispersant could have encouraged some flood tide movement of dispersed oil droplets up-estuary. Chemically dispersed oil from the *Sea Empress* was mostly transported away from the waterway and out to sea, but on flood tides oil naturally dispersed by waves and currents would have been transported into the waterway.

Using video taken on 22 February 1996 on behalf of CCW during a spill response over-flight arranged by ITOPF, oil sheens were observed and documented as far upriver as the Warrior jetty and the mouth of Cosheston Pill. This was one day after the final spill release during offloading of HFO from *Sea Empress* at the Herbrandston jetty. One month after the spill, during field sampling in March 1996 on behalf of the then newly-formed EA, some oil sheen on the subtidal sediment surface in the grab sampler was also observed in the low- to mid-estuarine reaches as far up-estuary as the mouth of Cosheston Pill (Hobbs[27]).

Shoreline oiling later in summer 1996 was also observed by trained CCW observers using the Shoreline Cleanup Assessment Technique (SCAT). On the north shore as far east as Llanstadwell and Neyland, and on the south shore as far east as Hobbs Point in Pembroke Dock, the total quantity of oil in this reach in 1996 was estimated from the codified visual assessment provided by SCAT to be less than 0.2 tonnes. This is only about 0.04% of the stranded oil (and <0.0003% of the total oil) released from the *Sea Empress* (Little[7], Arthur D. Little[26] and Little[28]).

Visible shoreline oil residues were reported almost a decade later in January 2006 at several locations within MHW (Figure 9): patches of weathered oil in the shelter of a rocky ridge at Kilroom and asphalt pavement along a section of shore in Pembroke River; oil traces were also found at Popton Beach, West Angle Bay, Dale and Pickleridge Lagoon (Moore[29]). Small patches of asphalt pavement associated with perched saltmarsh communities were observed in 2003 and 2004 in Sandyhaven Pill and Angle Bay; small patches of asphalt pavement and oil residues were noted for a few years along the upper shore in Martin's Haven near Pwllcrochan. Outside the estuary, an oily residue on upper shore bedrock persisted until at least 2000 at Hopgang and some locations in the Skomer Marine Nature Reserve; small amounts of oil were observed at Stackpole Head, St. Margaret's Island, in Tenby Harbour and on Tenby north beach until at least 1999. The locations with lingering visible oil residues are identified in Figure 9 (after Moore[29]).

In the MHW subtidal zone, only one set of pre- and post-*Sea Empress* PAH analyses was conducted, in October 1993 and October 1996. There was no significant change detected in average PAH or THC concentrations between these dates. The PAH suite analysed at the time did not permit a detailed determination of sources, but they were predominantly pyrogenic (Levell[30], Rutt[31]). The exception was in 1996 at five stations showing petrogenic influence and leading from the HFO spill source at the Herbrandston jetty eastwards along the sediment transport path in the main channel and northern shelf (Little[4] and McLaren[6]).

Using 27Ts and 27Tm biomarker ratios, it was shown that HFO affected lengthy sections of shore at Pwllcrochan and Angle Bay until at least June 1997 (Swannell[32]). At the latter site there were Forties blend and African crude oil biomarker fingerprints perhaps from earlier small spills in 1984 and 1992. Also, Angle Bay and Sandyhaven had been sites of a series of oil spill field experiments from 1979 to 1985 using Forties and Nigerian crudes (Little[3]). In contrast, at Kilroom/Mun Sands and two other stations outside the estuary only Forties blend was discernible. Following the *Sea Empress*, some hydrocarbon contamination lingered in intertidal areas studied by Swannell[32] in the lower MHW estuary. Upper shoreline oil was gradually eroded and probably recycled into the lower intertidal and subtidal zones, whence sediment transport probably removed the contaminated material in flood and ebb tidal streams leading into tributary bays and sub-estuaries (McLaren[6]).

In the intertidal zone, using ultraviolet fluorescence (UVF) spectrometry analysis of THC and comparing to a pre-*Sea Empress* baseline determined by Rostron[33] for samples taken in November 1994, it was found that patchy oil persisted in some of her 5 or 6 replicated intertidal sediment samples (Rostron[34]). Each of Pembroke River, Angle Bay and Sandyhaven Pill had elevated levels of Forties-equivalent oil. These lasted until at least April 1996 at Sandyhaven Pill (Pembroke River was discontinued after March 1996), and until March 1997 at Angle Bay. Unfortunately, no GC/FID or GC/MS forensic work was performed on these intertidal samples.

Monitoring using UVF in the subtidal zone was conducted for the EA after the *Sea Empress* incident. This showed that THC was elevated until October 1996 in Angle Bay and the lower estuary, but appeared to have returned to pre-spill benchmark levels by April 1997 throughout the estuary. The EA study found that THC levels continued to be low in these areas beyond April 1997, but that the THC increased again in the upper and mid-estuary in October 1997 (National Marine Monitoring Programme; NMMP[35]). Using these data, Nikitik and Robinson[36] suggested that a transient flush of

Sea Empress oil likely caused an impact on amphipods in MHW lasting up to 5 years. The second period of increased THC concentrations up-estuary could also be the effect of sediment disturbance by dredging campaigns in 1997 and subsequent transport of the contaminated sediment in flood tidal streams (McLaren[6] and Little[2]). As mentioned above, the visual occurrences and THC analyses were not confirmed forensically at the time. However, three of the above-mentioned data points (Pwllcrochan, Kilroom and Angle Bay) agreed closely with the fingerprinting done at the time of the spill by Swannell[32]. Furthermore, in the present forensic work all samples from Pembroke River, Angle Bay, Cosheston Pill and the main channel cluster with the SE Bunker reference samples in cluster (**A**) in Figure 8.

In contrast, the samples in cluster (**B**) of Figure 8 combine the sediment sampling locations that exhibit a biomarker signature similar to that of the Iranian heavy crude oil reference sample. These locations are from the upper estuary that had documented areas of heavy oiling shortly after the December 1988 *El Omar* spill at the Texaco (now Valero) terminal of approximately 100 t of Iranian light crude oil (Little[37]). About 20 t of chemical dispersants were used inside the estuary and this may have encouraged up-estuary oil droplet transport. Although no forensic PAH and biomarker work was carried out at the time, analyses by GC/FID showed a weathered crude oil fingerprint. Also, a review of sediment THC and GC/FID data collected in the upper estuary in April 1984 and April 1989 (before, and four months after, the *El Omar* spill) showed that aromatic hydrocarbons in Daucleddau subtidal sediments had increased significantly (t-test, $p<0.05$, n=31), perhaps as a result of *El Omar* (Little[37] and Little[4]).

Field and photographic evidence for limited incorporation of *El Omar* cargo into gravel intertidal sediments was collected in Angle Bay, Pembroke River and Pwllcrochan. Mixed muddier sediments were more heavily-oiled from east of Milford Haven, through Llanreath, Neyland, Barnlake, Cosheston Folly, to Garron Pill and Coedcanlas. Although no SCAT surveys were done to quantify the amount of oil the above observations represented, these mid- and upper-reaches of MHW were much more heavily-oiled by *El Omar* in 1988 than by *Sea Empress* in 1996. The salt marshes at the confluence of the rivers Carew and Cresswell received the majority of thick oiling (Figure 10). Sediment core samples were taken at this site, where it was found that oil that was trapped initially on *Spartina* leaves and stems in December 1988, was later transferred to the sediment, penetrating to about 8 cm depths by September 1989. Concentrations of oil reached about twice the highest levels registered in control cores (Little[37], Little[4]).

In addition to *El Omar* crude oil being a possible sediment contamination source in the innermost MHW, Iranian crude oil feedstocks have been processed in the refineries. Up-estuary transport of suspended sediments contaminated by weathered residues of Iranian crude(s) in refinery wastewater may have occurred over time. However, in terms of this interaction between long-term chronic inputs and fine-grained sediment transport processes, it would perhaps be expected that some other crude oil feedstocks in addition to Iranian crude would also have left their fingerprint in the upper estuary. As demonstrated above, source ratios of petrogenic PAH have detected some West African crude oils throughout MHW.

The sample from the Royal Fleet Auxiliary (RFA) *Darkdale* also shows many similarities to Iranian crude oil. She was carrying 3,000 t fuel oil refined at Curacao probably from Venezuelan (Maracaibo) crude oil feedstock before her sinking by U-68 in October 1941 at St. Helena in the South Atlantic during WW2 (ERT[12]). Apart from some lube oil, the only other cargo oils on-board were aviation gasoline (850 t), and diesel (500 t). She also refuelled *en route* to power her own engines. The use of HMS *Royal Oak* and RFA *Darkdale* material as reference samples in this study was simply to represent naval bunkers during WW2, and does not imply that the vessels visited Milford Haven during WW2. However, a possible wartime destination for both Venezuelan and Iranian crude-derived fuels would be the Admiralty tank farm at Llanreath near Pembroke Dock. Such mixtures of fuel oils could have been present in the inventory that was released from eleven storage tanks destroyed at Llanreath when this facility was bombed by the Luftwaffe on 19 August 1940. About 130,000 t of fuel oil was lost over 18 days of fires; some of it directly to the waterway by oil and firewater runoff, some by infiltration to groundwater. Most oil was burned and some of this was followed by aerial deposition both directly and indirectly, and transferred into MHW via runoff in subsequent overland flow. In addition to 5 fatalities among the 650 fire-fighters, crops were damaged by airborne pollutants in the hinterland, and even Devon (www.memories.thepenvro.com/Memories8A.html).

It is thus possible that all these sources may have contributed to the similarity of the oil contamination of upper estuarine sediments to an Iranian heavy crude fingerprint. However, there are as yet no known biomarker analyses of reference samples for *El Omar* cargo and the lost Llanreath tank farm inventory. For the latter, oil from the interceptor installed at Llanreath would suffice as a source reference sample for future work.

Until recently, only a sub-optimal selection of source ratios was available in the study area, given the scant PAH data (Little[4]). However, Figure 11 shows cross-plots of the PAH source ratios between 1993 and 2012 for BA/(BA+C), plotted against FL/(FL+ PY) (Yunker[19]). The diagram shows a difference between ratios pre- and post-*Sea Empress* in terms of the higher degree of petrogenic fingerprint at five stations in the lower estuary soon after the spill, as mentioned above. These stations are along the flood tide transport pathway on the northern shelf as was predicted using sediment trend analysis by McLaren[6]. Figure 11 also shows that there are overlaps between the pyrogenic material from dredged areas and the muddy tributaries sampled by the CCW survey in 2007 in support of their monitoring under the EU Habitats Directive.

The oval labelled (**A**) in Figure 11 represents the ratios' spread, both for November 2010 from ERT[12], and for October 2012 from CCW's more recent survey. These ratios show good comparability between CCW and ERT datasets, in spite of method differences between surveys. The source ratios are close in spite of significant reductions in PAHs concentrations (sum of up to 29 comparable PAH) between 2007 and 2010 (t-test,

$p<0.01$, n=12). In contrast, there were no significant differences between 2010 and 2012 for both the sums of 29 and of 37 comparable PAH concentrations, in spite of the fact that they were generated by different laboratories.

Table 4 summarises CCW data for 2007 and 2012, showing that trends in concentrations of heavy metals and other contaminants generally corresponded to the above observations for PAHs, notably the much higher concentrations in 2007. Again, this strengthens confidence in the comparisons of PAHs data from different laboratories. The fact that the concentrations of six heavy metals, TBT and total PAHs all decreased between 2007 and 2012 suggests that changes in the various laboratory procedures cannot alone explain the results. Grain size (% finer than 63 μm) and organic content changes were small (non-significant increases), and thus would not have caused the observed decreases in contaminants from 2007 to 2012.

Although PAH concentrations have decreased, the source ratios for ERT 2010 and CCW 2012 PAH are still quite similar to those from CCW 2007. This is shown in Figure 11 by overlaps between the ovals labelled respectively (**A**) and (**B**). The spread of ratios suggests a slight petrogenic trend that extended down-estuary, and generally a more pyrogenic fingerprint up-estuary, as had been found in 1993 and 1996. The ratios for both 2010 and 2012 cluster more at the highly-pyrogenic right-hand side of the CCW 2007 (**B**) oval. They are also mostly within the 2001-2006 cluster represented by oval (**C**) containing berthing box sediment data from the dredging licensing work by the Centre for Environment, Fisheries and Aquaculture Science (CEFAS). The reason for this pattern was probably the continuing return to domination by pyrogenic sources in contrast to the lingering of earlier petrogenic inputs from the *Sea Empress* in 1996. However, it should be re-emphasised that the dominant PAH signature has been pyrogenic since October 1993 (Figure 11).

More recent CEFAS dredging data for 2008, 2009 and 2012 (Figure 11, rounded rectangle **D**) show source ratios with far wider scatter than any discussed above, partly because they include samples from Pembroke Port (Ro-Ro), Milford Shelf and (for 2008 only) the new power station channels, both intake and outfall. However, these recent data included some from Chevron berths in both 2009 and 2012. These ratios are also far more widely scattered than those from any of the samples taken from here or the other refinery terminal berths in 2001-2006 and shown within oval **C** (Figure 11). This suggests that sediments deposited in the Chevron berths between 2006 and 2012 originated from more varied, albeit still pyrogenic, sources than was the case prior to 2006. In fact, the ratios within **D** overlapped more closely with samples of 1993 pre-*Sea Empress*, 1996 pyrogenic post-*Sea Empress*, one of the bioaccumulation samples (described below, Langston[38]), and with samples from Associated British Ports (ABP, personal communication). This ABP sample was taken in 1995 outside MHW and shows a possible return pathway for PAH transfer into MHW from a dredge spoil disposal site that is now disused. The inclusion of the majority of 1993-1996 source ratios in this group with CEFAS 2008-2012 ratios (Figure 11, rounded rectangle **D**) suggests resuspension of un-dredged older material by construction activities outside of the berthing boxes and channels that are regularly dredged.

Further comparison of PAH composition was made between the 2010 ERT data and the October 2012 CCW data. In Figures 12 and 13 the source ratio cross plot data for 2012 are superimposed on those shown in Figures 5 and 6 respectively for 2010. Also shown for comparison in Figure 12 are source ratios calculated from the following: Clean Seas Environment Monitoring Programme (CSEMP[39]) PAH data for sediment samples from Cosheston Point 1999-2011; Department for Environment, Food and Rural Affairs (Defra[40]) air quality PAH data for Newport and Port Talbot 1999-2006; and bioaccumulation data for mussels *Mytilus edulis* and ragworms *Nereis diversicolor* at Dale, Angle and Pennar in Pembroke River in 2010 (Langston[38]).

The PAH source ratios for MHW sediments in 2010 and 2012 all show tight clustering and indicate pyrogenic sources dominated by biomass and coal combustion (Figure 12). In the annual CSEMP survey off Cosheston Point the fingerprint is similar to the above but more scattered for some years. A source including petroleum combustion is indicated by ratios against FL/(FL+PY) of AN/(AN+P) in 2004, and of IN/(IN + BPE) in 2000 and 2011. In 2003, the former ratios approached that of the NMMP (now CSEMP) station 646 in 1996, which was a site possibly contaminated by *Sea Empress*.

The PAH source ratios of South Wales air samples analysed nationally on a quarterly basis by Defra between 1999-2006 do not overlap with the sedimentary PAH in MHW, with the exception of FL/(FL+PY) *vs.* IN/(IN + BPE) in 2005 and 2006 in Newport. This apparent coupling of aerial inputs and sedimentary PAH reflects local combustion and runoff of road fuel particulates. Emissions peaked around 2007 just before the economic downturn, since when they have declined by about 8%, based on Office of National Statistics data on local Pembrokeshire and UK road fuels consumption (www.ons.gov.uk/). Yet the timing of the relationship with PAH source ratios in MHW possibly also reflects longer-range inputs in late 2005 and early 2006 from the major accident and fire (56,000 t burned) at the Buncefield oil storage depot in Hertfordshire on 11 December 2005 (Little[5]).

As would be expected in an iron and steel manufacturing area, most ratios in Port Talbot were skewed to coal combustion sources (Figure 12). In contrast to the slight decrease in the bioaccumulation data generally, the mussels at Angle and Pennar showed a pronounced increase in the sum of 16 PAHs between early 2008 and 2010 (Langston[38]). This extra bioaccumulation in mussels agreed closely with sediment sample trends from late 2007 to 2010 at the two sites, and is consistent with the timing of known periods of sediment disturbance, notably the construction period of the nearby power plant between 2008 and 2011 (Little[5]).

There are some quite significant discrepancies in individual PAH concentrations between the ERT 2010 and CCW 2012 datasets that may be at least partially due to the difference in analytical procedures employed by the laboratories. Also, no biomarker analyses were conducted in the 2012 study for CCW. However, the absolute values are not so important from the strictly forensic point of view, because the forensic interpretations are based primarily on ratios.

A check on some of the key ratios shows that those that involve only parent (not alkylated) PAH compounds are in good agreement between ERT 2010 and CCW 2012 datasets (Figure 12). There is, however, a noticeable systematic shift in the ratios based on alkylated PAH compounds C2D/C2P and C3D/C3P (Figure 13). This is probably a function of the initial data used for calculating the alkylated PAH ratios, for most of which authentic standards of PAH compounds are not available. The ERT ratios for the field samples and the reference sample standards were calculated based on the chromatographic peak areas, whereas for the CCW ratios absolute analyte concentrations were used.

In any case, the shift in alkylated PAH ratios does not change the conclusions regarding the source(s) of PAH contamination in MHW sediments. For example, even with the alkylated PAH shift, it can be clearly seen that CCW 2012 data are still clustered in the same general area of the source ratio plots as the ERT 2010 data (Figure 13). The CCW data are closer to the Bonny crude reference than were the ERT data. However, if all the data points are combined, these cross plots of petrogenic PAH ratios clearly support the conclusion that sediment contamination by petrogenic PAH is most similar to refinery effluent and Africa-sourced crude oils. Indeed, the explanation for the PAH source ratios' shift is likely the increased throughput and contribution via treated effluent discharges of Africa-sourced crude oils in the two years between 2010 and 2012. For example, at Murco (MHWESG member, personal communication) there has been increased use since 2010 of feedstocks from West Africa (Nemba, Agbami, Kissanje, Erha, Bonny, Escravos, Akpo, Brass River, Qua Iboe and Palanca) and North Africa (Mellitah, Zarzaitine and Zueitina).

Considering the above-mentioned changes in PAH concentrations through time, we interpret these in terms of new contaminant inputs (aerial, runoff, effluent and any small spills) to surficial sediments, in combination with the disturbance of subsurface sediments historically-contaminated by oil and metals. We suggest that periodic dredging and construction disturbance of sediments have released plumes of fine-grained silt and clay that were transported into sedimentary sinks and filter feeding biota in MHW. Peaks in these activities are reflected in high sediment contaminant concentrations and by forensic evidence linking sources and sinks, supported by sediment trend analysis (Little[5]). In combination with peak inputs from the atmosphere due to increasing use of diesel fuels (before the economic downturn) and possible fallout from Buncefield, the sediment disturbance peak in 2006 appears to have caused a "perfect storm" in MHW sediment contaminants by 2007.

Support for the hypothesis that dredging and construction are responsible for some of the disturbance comes from visual evidence from sediment profile imagery (SPI) obtained at 559 stations in MHW in May 2012 (Germano[41] and Carey[42]). High-resolution SPI shows stratified sediments with winnowed sands overlying mud at a small subset of stations near the main channel in the mid-reaches of MHW down-current on ebb- and flood tides from where dredging and construction were concentrated (Figure 14). The sediment suspensions resulting from such disturbance exceed the typical baseline conditions estimated from turbidity levels in MHW (Little[5]). Candidate sources include maintenance and other dredging works, site clearance and construction of two LNG terminals, pipelines and a new power plant. The following peak periods of sediment runoff, disturbance and resuspension occurred:

1. LNG-related construction: South Hook LNG ground works included contaminated land at former Esso refinery site in 2003-2005; marine jetty pile driving and peak refurbishment from late 2005 to end 2008, particularly years 2006-2007; South Hook LNG capital dredging took place in 2006; Dragon LNG started jetty refurbishment in March 2006 and completed in March 2007; and Pembroke Power Station construction was 2010-2011
2. Port of Milford Haven maintenance dredging using trailing suction hopper dredger, with any hopper spillage peaking in 2006 and 2010
3. Neyland Yacht Haven dredging using cutter suction dredger causing mud suspensions with peak disposals directly into MHW in 2005, 2007-2009, and 2011.

The timing of observed chemistry and biological impacts, peaking in 2007 but with subsequent partial recovery, appears to be coincident with the relatively recent sediment disturbances listed above. Probable biological effects in 2007 were predicted using sediment quality guidelines (*e.g.* USA's National Oceanic and Atmospheric Administration, and Environment Canada). According to Little (5) this 2007 peak is consistent with troughs in long-running biological monitoring data at Dale, West Angle Bay and the mouth of MHW. PAH bioaccumulation in mussel *Mytilus edulis* in Angle Bay and Pembroke River between late 2008 and 2010 showed the slightly later effects of the power plant construction (Langston[38] and Little[43]).

The impacts described in this forensics study were not detected using fully standardised methods within a strict experimental design. The independent and supporting work in sedimentology and biology was not included by design, other than being among the monitoring recommendations made in a review of sediments for MHWESG (Little[4]). Although the laboratories were not always the same, cross-checks were made against existing NLS data before and after 2010, and by observing consistency of trends between organics and metals contaminants. The study is believed to compare favourably to work of this sort in MHW or elsewhere. It was the first wide-scale study in MHW (up to 19 sites) using advanced methods for chemical fingerprinting (37 PAHs plus proven biomarkers), and 18 reference and source samples analysed alongside the environmental samples.

With the two exceptions of sediment tracer studies at Neyland Yacht Haven and a plume of mud predicted to spread into Pembroke River from construction of the intake channel at RWE npower, the described impacts had not been predicted by any MHW environmental impact assessment (EIA) seen by the present authors. More generally, this could mean that dredging disturbance and impacts may be greater than typically predicted in EIAs, where impacts at the disposal site tend to receive more attention than those near the dredging itself. The short duration of the impacts also meant that they were not picked up by the regular surveillance programmes. The routine MHW oil spill incident reports in several years before 2007 do not suggest any reason for the peak contaminant concentrations registered in that year. Similarly, the decline since 2007 of about 8% in probable road fuel emission inputs does not explain fully the decreased contaminant concentrations since that year.

Without the three closely-spaced surveys of PAH in 2007, 2010 and 2012, the peak contaminant concentrations in 2007 across the entire MHW would not have been seen as the pronounced but ephemeral event that it was. Impact identification might not have been possible or reliable if sampling had not been done by the same people, at the same stations, same time of year, and focussing on the surficial sediment layers consisting of recent deposits most likely deriving from resuspended contaminated material.

The results of this study should not necessarily be interpreted as a calamity for MHW. Other monitoring work on rocky shore and sediment benthos suggests biological communities maintain their diversity and functional integrity (*e.g.* Warwick[44], Bullimore[45]). The resuspension of contaminated muddy sediments by storm waves on peak spring tides or by dredging operations affects the release and bioavailability of contaminants (Eggleton[46]). Although typically assumed to be a process with adverse effects, the resuspension of anoxic fine-grained sediments by dredging also allows aeration, desorption and biodegradation of contaminants, before the mud plume settles elsewhere. Provided it is not excessive in space and time, whereby released pore waters and fine particles could have acutely toxic impacts on water column species, a well-managed dredging programme is both economically necessary and environmentally sustainable in MHW.

Conclusions

Current and historic petroleum-related activities in MHW have contributed to the hydrocarbon contamination of surficial sediment in the study area, and these contaminant inputs have evidently involved up-estuary sediment transport processes, often over long time periods. The environmental forensic investigation demonstrates that the sediment hydrocarbon contamination consists of three major components: n-alkanes of a predominantly biogenic nature, PAH compounds of mixed sources (more recent petrogenic and older pyrogenic), and a major part of THC predominantly attributed to the heavily weathered historic spills and to a lesser extent petrogenic oil-industry related contamination. The following key findings support this conclusion:

1 Gas chromatographic characteristics of hydrocarbon contamination with a dominant UCM signal are indicative of a relatively high degree of petroleum weathering, and suggest that old pollution events are the most likely source of the majority of hydrocarbon contamination (70-85% of THC).

2 The presence of resolved n-alkane peaks in the n-C_{21} - n-C_{35} range with a predominance of odd-carbon-number hydrocarbons, is typical of mainly biogenic sources of n-alkanes in the surficial sediment of the MHW (5-15% of THC).

3 Analysis of aromatic compounds revealed a minor contribution of the lower-molecular-weight, 2- and 3-ring PAH compounds with a typical petrogenic profile. A moderately-weathered signature of these contaminants suggests a relatively recent source of petrogenic PAH in the MHW.

4 The treated refinery oily effluent appears to contribute to this more recent petrogenic PAH compounds, with possible additional impact from African-sourced crude oils that have been increasingly processed at the local refineries. The target PAH compounds constitute 2-6% of THC in sediment. Considering that the petrogenic portion is no more than half of total PAH, a rough estimate for the recent petrogenic contribution from the refinery waste water (and potentially from some African crude oils) is about 1-3% of THC.

5 The elevated content of higher-molecular-weight, 4-, 5- and 6-ring PAH compounds and descending distribution patterns of fluoranthene/pyrene and chrysene homologous series are typical of pyrogenic sources. The evaluation based on the PAH source ratios demonstrates that these pyrogenic PAH compounds in the surficial sediments predominantly originate from biomass (grass and wood) and coal combustion.

6 The evaluation based on the biomarker source ratios demonstrates that most of the THC contamination in the main channel and low- and mid-section of the MHW is most probably related to the heavily-weathered HFO bunker oil spilled during the 1996 *Sea Empress* accident. The forensics fingerprint extends by at least 2 km up-estuary and by 13 years the contamination footprint of *Sea Empress* HFO that previously had been documented.

7 The biomarker signature suggests that a major fraction of the sediment hydrocarbon contamination in the upper reaches and tributary estuaries is from three possible sources: lingering impact from the 1988 *El Omar* spill, Iranian crude feedstock supplied to local refineries and WW2 Llanreath fuel oil mixtures lost in the 1940 air raid fires. These sources cannot yet be confirmed due to lack of corresponding reference samples.

8 The PAHs consist of similar pyrogenic PAH at most stations. These are likely transferred *via* resuspended sediments that have been disturbed or spilled by dredging (or disposed of inside MHW in the case of one marina site). Sediment PAHs at some stations appear to have become progressively more pyrogenic from 1996 to 2012, as if still recovering from the more petrogenic signature from the *Sea Empress*.

9 The main findings of the three surveys discussed in this study were reasonable when compared with other PAHs surveys: (1) before and after the *Sea Empress* spill in 1996; (2) CEFAS licensing of maintenance dredging for port, navigation channels and berthing boxes; (3) CSEMP independent annual surveys since 1999 off Cosheston Point; (4) Defra quarterly surveys since 1999 of air quality at two stations in South Wales; and (5) bioaccumulation data from Angle and Pennar for

ragworms and mussels between 2007/2008 respectively, and 2010.

10 The pyrogenic PAH ratios and the total PAH concentration changes through time using the CCW data before and after the 2010 MHWESG survey together underpin the 2010 findings. The % mud and organics were unchanged, and heavy metals concentrations declined between 2007 and 2012. These findings also endorse those for the PAHs.

11 The detailed forensic analyses of 2010 data have identified PAHs from present-day refinery effluent and from historic sources: the *Sea Empress* HFO, and possibly from *El Omar* and WW2 tank-farm fires. Domination of fingerprints in the surficial (<2 cm deep) sediments across the waterway by the historic pollution sources strongly suggests disturbance of settled sediments, most likely by construction and dredging.

The study also shows that the shoreline cleanup assessment technique (SCAT) and aerial reconnaissance combined with advanced forensic analyses are very powerful, not only at the time of an initial spill response (*e.g. Sea Empress*), but also in longer-term determinations of the biota's exposure to the spilled oil and the apportionment of multiple sources in industrialized waterways like MHW. They help to facilitate a fuller and more technically defensible assessment of the ecological impact of the incidents (*e.g.* both *Sea Empress* and *El Omar*) and of major engineering works. The geochemical markers effectively act as sediment tracers that substantiate sediment and contaminant transport patterns predicted previously for MHW using sediment trend analysis.

MHWESG members should collectively ensure that forensic-quality analyses of stored reference samples are a part of the standard approach to response and monitoring after significant spills and engineering works in MHW. This quality control may not be best left to a sequence of contractors. Closer collaboration between MHWESG members in their various individual monitoring activities would help to overcome any changes in personnel, methods and laboratory. Additionally, the suites of PAHs and trace elements that are being monitored have changed over time, and this could be strengthened in future monitoring.

The sediments analysed in this study were surficial, sampled from <2 cm deep in accretional areas, which is most useful for monitoring purposes. Knowledge of the interplay between current and historic contaminant inputs would be greatly enhanced by hydrocarbon chemical fingerprinting of sediment depth sections from carefully-located, radionuclide-dated cores. Whereas previous dated core studies in the late 1980s were useful at the time, they did not employ advanced forensic methods (including PAHs and biomarkers), some of which were only developed after the 1989 *Exxon Valdez* incident. Future analyses of coal from local derelict collieries and of recovered oil from the interceptor at the Llanreath oil storage tank site should be used as historic reference samples, to be examined alongside the dated cores.

The forensics study has established the broad similarity of PAH distributions in MHW, and shown their persistence since before WW2. Pyrogenic PAHs outweigh petrogenic sources, perhaps surprising in a major oil port, but consistent with their recalcitrance in marine sediments. In spite of *Sea Empress* being the third largest UK oil tanker spill and in the top twenty worldwide, no positive identification was made of her crude oil cargo, only the bunkers, also consistent with the recalcitrance of HFO.

Acknowledgements

This paper is based on survey data commissioned by MHWESG. We acknowledge members who provided reference samples of oils and effluents, and feedstocks data. The 2010 data for sediment and reference samples were supplied under contract to MHWESG by ERT, following recommendations by Little[4].

ERT provided additional reference samples from their archives, and we thank G. Todd and his team. Likewise, our appreciation goes to Natural Resources Wales for the NLS data for 2007 and 2012, and also to their fieldwork team in all surveys.

We thank J. Germano and D. Carey for SPI data and also R. Law for help accessing the MERMAN data (Cosheston Point) which were supplied by the British Oceanographic Data Centre on behalf of the Clean Safe Seas Evidence Group. The manuscript was improved by two anonymous reviewers.

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Table 1 Sediment samples collected in 2010, and reference oil samples analysed

Sample ID	**% mud (2007)**	**Station location**	**Latitude/ longitude or Ordnance Survey**
Tributary estuary sediment samples:			
SHU	0.50	Sandy Haven Upper	*Not selected for sampling - not fine-grained*
SHL	3.30	Sandy Haven Lower	*Not selected for sampling - not fine-grained*
AH	70.63	Angle Harbour	N51.6834°, W5.831°
AB	23.81	Angle Bay	N51.6827°, W5.7224°
PRU	52.39	Pembroke River Upper	N51.6785°, W4.9522°
PRL	85.78	Pembroke River Lower	N51.6806°, W4.9659°
CPU	85.98	Cosheston Pill Upper	N51.6947°, W4.9063°
CPL	Not determined	Cosheston Pill Lower	N51.6968°, W4.9181°
CARL	80.53	Carew River Lower	N51.7123°, W4.859°
CRRU	65.70	Cresswell River Upper	N51.723°, W4.8332°
CRRL	37.69	Cresswell River Lower	N51.7213°, W4.8757°
WCU	93.39	Western Cleddau Upper	*Not selected for sampling – time constraints*
WCL	55.38	Western Cleddau Lower	N51.7713°, W4.9243°
ECU	56.76	Eastern Cleddau Upper	N51.7901°, W4.8379°
ECL	37.53	Eastern Cleddau Lower	N51.7725°, W4.8788°
VC23	98.10 (2010)	Pennar Gut	OS Easting 193872.1, Northing 202638.7
VC24a/1	95.80 (2010)	Pennar Gut	OS Easting 194101.3, Northing 202674.6
Main channel sediment samples:			**Latitude/ longitude**
MH4	45.30 (2008)	Off Mine Depot jetty	N51°42.020', W5°00.8215'
MH10	92.10 (2008)	Off Llanreath	N51°41.754', W4°58.2155'
Reference source oils and samples:			**Comments**
Agbami crude (Nigeria)			Density 0.789, supplied by MHWESG
Amna crude (Libya)			Density 0.840, supplied by MHWESG
Captain crude (heavy North Sea)			Density 0.932, supplied by MHWESG
Forties crude (North Sea)			Density 0.827, supplied by MHWESG
Refinery Waste Water Treatment Plant (RWWTP) sample			Final effluent, supplied by MHWESG
Sea Empress bunker			Supplied by ERT
Sea Empress cargo			Supplied by ERT
Sea Empress Forties crude			Supplied by ERT
Sea Empress fourth bunker			Supplied by ERT
Sea Empress Newgale beached			Supplied by ERT
RFA *Darkdale* fuel oil cargo ex-Venezuela			Sunk WW2 St. Helena, supplied by ERT
HMS *Royal Oak* bunker oil			Sunk WW2 Orkney, supplied by ERT
Bonny crude (Nigeria)			Supplied by ERT
Brent crude (North Sea)			Supplied by ERT
Iranian heavy crude			Supplied by ERT
Iranian light crude			Supplied by ERT
Kuwait crude			Supplied by ERT
Venezuelan crude			Supplied by ERT

[Notes: Field samples were surface sediment (<2 cm depth) scoops taken from grabs or cores. Samples from MH4 and MH10 were collected specifically for MHWESG during Environment Agency (EA) grab sampling in early April 2010. GTS Subsea[13] provided vibrocore samples taken 9-10 August 2010 from stations VC23 and 24a/1 in Pennar Gut for Jacobs Engineering Ltd on behalf of MHWESG member RWE npower. All other field samples were collected by CCW specifically for MHWESG as contribution in kind from 3-5 November 2010. Percentages of mud (<63 µm particle diameter) in 2007 and 2008 were determined by the EA's National Laboratory Service (NLS), and in 2010 by Geolabs for Jacobs Engineering Ltd.]

Table 2 Sediment individual PAH concentrations (ng/g) and biomarker ratios, MHW 2010

Station ID	AH	AB	PRU	PRL	CPU	CPL	CARL	CRRU
Naphthalene	202	49	136	174	143	124	28	54
C_1 - Naphthalene	389	129	258	343	269	225	94	183
C_2 - Naphthalene	763	286	489	630	498	430	166	318
C_3 - Naphthalene	777	277	445	571	430	396	86	175
C_4 - Naphthalene	408	146	245	311	211	212	49	93
Fluorene	255	49	134	175	139	121	26	51
C_1 - Fluorene	247	55	142	185	132	124	26	46
C_2 - Fluorene	302	69	199	224	164	167	35	65
C_3 - Fluorene	250	60	164	177	141	141	24	47
Phenanthrene	1150	207	539	612	499	534	89	196
Anthracene	253	38	126	143	117	166	20	39
C_1 - Phenanthrene/Anthracene	1210	234	704	733	584	632	149	298
C_2 - Phenanthrene/Anthracene	1580	322	985	994	778	877	162	294
C_3 - Phenanthrene/Anthracene	1010	198	678	656	507	648	127	183
C_4 - Phenanthrene/Anthracene	538	93	314	405	306	531	135	106
Dibenzothiophene	109	23	61	78	61	57	15	29
C_1 - Dibenzothiophene	138	32	84	105	81	76	20	39
C_2 - Dibenzothiophene	168	39	112	142	102	101	21	37
C_3 - Dibenzothiophene	122	28	90	120	78	83	19	33
Fluoranthene	1720	205	818	730	676	796	161	392
Pyrene	1300	159	652	631	595	647	136	303
C_1 - Fluoranthene/Pyrene	957	121	520	534	460	557	118	237
C_2 - Fluoranthene/Pyrene	530	80	324	393	281	345	104	193
C_3 - Fluoranthene/Pyrene	317	56	223	297	190	244	91	159
Benz[*a*]anthracene	950	104	493	482	405	486	83	198
Chrysene	1160	138	626	656	528	613	101	248
Benzo[*b*]fluoranthene	1020	137	606	677	535	555	145	337
Benzo[*k*]fluoranthene	331	42	192	223	161	186	44	104
Benzo[*e*]pyrene	623	84	370	445	317	350	90	209
Benzo[*a*]pyrene	528	65	289	380	245	291	68	172
Perylene	199	28	124	151	95	118	37	71
Indeno[123-*cd*]pyrene	368	52	253	374	224	233	64	164
Benzo[*ghi*]perylene	254	38	187	314	154	179	40	116
Dibenzo[*ah*]anthracene	92	12	62	98	55	59	14	39
29ab/30ab	0.839	0.827	0.863	0.970	0.861	0.881	0.827	0.847
27Ts/27Tm	0.689	0.738	0.749	0.787	0.625	0.807	0.758	0.767
C20TA/C21TA	0.919	0.813	0.785	0.823	0.835	0.775	0.22	0.340

[Source: ERT[12]]

Table 2 Sediment PAH concentrations (ng/g) and biomarker ratios, MHW 2010 (continued)

Station ID	**CRRL**	**WCL**	**ECL**	**ECU**	**VC23**	**VC24a/1**	**MH4**	**MH10**
Naphthalene	47	20	14	45	75	69	140	106
C_1 - Naphthalene	153	43	39	147	201	185	230	194
C_2 - Naphthalene	269	76	84	273	350	319	422	302
C_3 - Naphthalene	144	49	59	147	219	202	389	241
C_4 - Naphthalene	82	28	29	84	115	100	196	127
Fluorene	47	24	19	50	63	58	156	81
C_1 - Fluorene	40	13	13	42	51	48	142	86
C_2 - Fluorene	57	21	20	64	81	76	162	105
C_3 - Fluorene	42	20	15	53	68	57	126	94
Phenanthrene	196	105	70	189	190	185	664	297
Anthracene	44	28	28	41	44	41	187	69
C_1 - Phenanthrene/Anthracene	275	122	113	267	321	322	682	348
C_2 - Phenanthrene/Anthracene	286	158	140	291	447	427	933	485
C_3 - Phenanthrene/Anthracene	183	115	89	209	358	331	649	347
C_4 - Phenanthrene/Anthracene	142	80	50	130	254	209	392	161
Dibenzothiophene	26	11	10	28	25	25	65	45
C_1 - Dibenzothiophene	33	14	14	38	51	50	72	58
C_2 - Dibenzothiophene	33	20	15	43	68	59	96	75
C_3 - Dibenzothiophene	29	22	31	48	80	61	82	64
Fluoranthene	373	264	175	415	250	246	803	328
Pyrene	296	203	136	317	208	208	646	303
C_1 - Fluoranthene/Pyrene	241	136	104	248	204	201	511	235
C_2 - Fluoranthene/Pyrene	197	87	82	200	202	201	306	163
C_3 - Fluoranthene/Pyrene	154	63	54	168	195	184	203	117
Benz[*a*]anthracene	197	117	92	206	112	120	453	201
Chrysene	242	134	99	264	166	170	545	255
Benzo[*b*]fluoranthene	320	182	126	353	260	244	545	273
Benzo[*k*]fluoranthene	106	51	41	109	72	72	182	86
Benzo[*e*]pyrene	197	106	79	214	160	157	343	177
Benzo[*a*]pyrene	156	71	65	167	86	94	330	158
Perylene	69	39	33	160	163	90	129	67
Indeno[123-*cd*]pyrene	139	58	54	158	93	103	254	133
Benzo[*ghi*]perylene	90	32	40	107	50	63	215	114
Dibenzo[*ah*]anthracene	33	13	13	38	19	22	64	34
29ab/30ab	0.892	0.875	0.849	0.883	0.886	0.836	0.869	0.832
27Ts/27Tm	0.735	0.713	0.685	0.755	0.783	0.805	0.721	0.708
C20TA/C21TA	0.119	0.163	0.004	0.144	0.920	0.829	0.789	0.751

[Source: ERT[12]]

Table 3 Selected ratio values for reference samples

Reference ID	C2D/C2P	C3D/C3P	27Ts/27Tm	29ab/30ab	C20TA/C21TA
Agbami crude	0.143	0.136	2.111	0.511	2.166
Amna crude	0.13	0.139	1.4	0.527	1.212
Captain crude	0.435	0.473	1.598	0.419	1.032
Forties crude	0.577	0.569	0.918	0.421	1.097
RWWTP sample	0.237	0.279	1.015	0.614	1.047
Sea Empress bunker	1.056	1.209	0.591	0.895	0.974
Sea Empress cargo	0.574	0.479	1.17	0.432	1.506
Sea Empress Forties crude	0.481	0.432	1.143	0.445	1.133
Sea Empress fourth bunker	1.085	1.176	0.621	0.869	1.085
Sea Empress Newgale beached	0.881	0.85	1.069	0.462	1.126
RFA *Darkdale* fuel oil cargo	2.221	2.15	0.73	0.998	1.693
HMS *Royal Oak* bunker oil	0.39	0.397	0.743	0.574	1.153
Bonny crude	0.207	0.17	0.741	0.606	0.157
Brent crude	0.489	0.426	1.109	0.413	0.929
Iranian heavy crude	1.729	1.469	0.783	0.702	0.142
Iranian light crude	1.911	1.867	0.689	1.01	1.368
Kuwait crude	2.023	2.519	0.36	1.353	1.628
Venezuelan crude	3.521	3.54	0.511	1.384	0.249

[Source: ERT[12]]

Table 4 Summary CCW sediment chemistry data for Milford Haven, 2007 and 2012

Station	**Mud %**		**OC %**		**TBT μg/kg**		**Hg mg/kg**		**Cd mg/kg**		**Cr mg/kg**		**Cu mg/kg**		**Pb mg/kg**		**Zn mg/kg**		**ΣPAH29 mg/kg**		**ΣPCB7 μg/kg**	
Date	**2007**	**2012**	**2007**	**2012**	**2007**	**2012**	**2007**	**2012**	**2007**	**2012**	**2007**	**2012**	**2007**	**2012**	**2007**	**2012**	**2007**	**2012**	**2007**	**2012**	**2007**	**2012**
SHU	0.5	<0.01	<0.4	0.95	<3	<3	0.006	0.005	0.025	0.025	9.91	10	4.93	1.59	4.13	4.05	23	21.3	0.27	0.02	<0.1	<0.1
SHL	3.3	6.25	<0.4	1.05	<3	<3	0.008	0.009	<0.01	0.033	8.93	27.2	8.15	2.61	5.11	6.3	26.1	30.2	1.82	0.15	<0.1	<0.1
AH	70.63	87.22	1.4	1.81	9	<5	0.192	0.117	0.2	0.182	50.2	40.3	28.3	23.4	48.9	44.6	149	141	15.6	4.66	0.29	3.64
AB	23.81	30.75	<0.4	0.92	<3	<3	0.02	0.022	0.08	0.068	21.4	15.1	5.54	5.62	10.3	11.6	46.5	50	4.97	0.77	<0.1	0.16
PRU	52.39	34.04	1.26	1.42	<3	<4	0.14	0.094	0.171	0.181	48.3	27.4	23.3	15.8	36.1	32.6	116	106	8.02	11.44	<0.1	1.32
PRL	85.78	80.08	1	1.27	8	<4	0.126	0.098	0.172	0.138	42.5	31.7	22.3	19.4	36.6	36.6	118	118	10.7	3.14	<0.1	1.64
CPU	85.98	81.17	1.04	2	<3	<4	0.144	0.129	0.2	0.161	35.4	28.5	19.9	16.8	37.4	35.7	119	109	12.4	5.11	2.72	0.48
CPL	63.61	62.97	1.03	1.08	20	<4	0.102	0.118	0.173	0.136	39.2	26.1	19.5	14.3	34.5	28.3	126	102	15.3	2.97	<0.1	1.44
CARL	80.53	80.06	1.11	1.61	8	<4	0.243	0.112	0.404	0.208	66.7	32	38.1	20.3	66.7	37.1	220	127	10.4	4.71	<0.1	1.56
CRRU	65.7	80.61	1.9	1.82	<3	<5	0.152	0.127	0.358	0.288	47.6	32.9	59.6	24.5	38	39.2	151	143	17.8	3.78	0.12	1.36
CRRL	37.69	68.38	2.16	1.51	<3	<4	0.124	0.141	0.313	0.248	50.7	30	26.4	21.7	39.9	37.1	150	131	18.7	4.7	<0.1	1.52
WCU	93.39	85.72	2.28	2.48	<3	<6	0.172	0.149	0.529	0.424	75.8	39.5	49.8	31.1	50.4	44.3	209	186	15.95	4.23	<0.1	1.84
WCL	55.38	74.65	2.22	1.21	<3	<5	0.114	0.121	0.341	0.325	47.5	31.6	25.1	22.2	33.7	35.2	143	148	4.17	3.37	<0.1	0.8
ECU	56.76	78.73	2.04	2.41	9	<5	0.18	0.115	0.454	0.35	63	36.7	32.2	25.2	41.4	36.3	189	157	12.84	5.91	<0.1	1.48
ECL	37.53	55.53	1.1	1.59	<3	<4	0.083	0.065	0.206	0.185	32.6	23.8	15.8	14.4	24.4	23.8	114	110	11.09	2.74	<0.1	0.4

[Source: National Laboratory Service raw data from CCW 2007 and 2012 surveys: Contains Natural Resources Wales information © Natural Resources Wales and database right]

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Figure 1 Milford Haven Waterway fine-grained sediment sampling locations (see also Table 1)

Figure 2 Gas chromatogram of Forties crude oil reference sample (peaks A, B, C and D correspond to laboratory internal standards)

Figure 3 Representative gas chromatogram of MHW sediment (Sample CPL see Table 1; * = uncharacteristically abundant peaks in the retention time window of n-C_{17} and pristane clearly reflect matrix interference rather than target analytes; peaks A, B, C and D correspond to laboratory internal standards)

Figure 4 Representative PAH distribution pattern in MHW sediment (Sample MH4)

Figure 5 Cross-Plots of PAH source ratios: (A) AN/(AN+P) vs. FL/(FL+ PY); (B) BA/(BA+C) vs. FL/(FL+ PY); (C) IN/(IN + BPE) vs. FL/(FL+ PY)

Figure 6 Cross-plot of petrogenic PAH source ratios in MHW sediments (ratios for reference samples SE Bunker, Iranian, Kuwait and Venezuelan crude oils, and RFA *Darkdale* are >1 and not shown in the plot)

Figure 7 Cross-plot utilizing terpane source ratios in MHW sediments

Figure 8 Cross-plot of terpane and triaromatic sterane source ratios in MHW sediments

Figure 9 Small areas visibly-affected by *Sea Empress* oil (after Moore[29]), compared to the uppermost extent of shoreline oiling in MHW during 1996 (★= grounding site in February 1996; red dots indicate oil residues reported in 2006; ⬮= inside waterway, and ⬬= outside waterway)

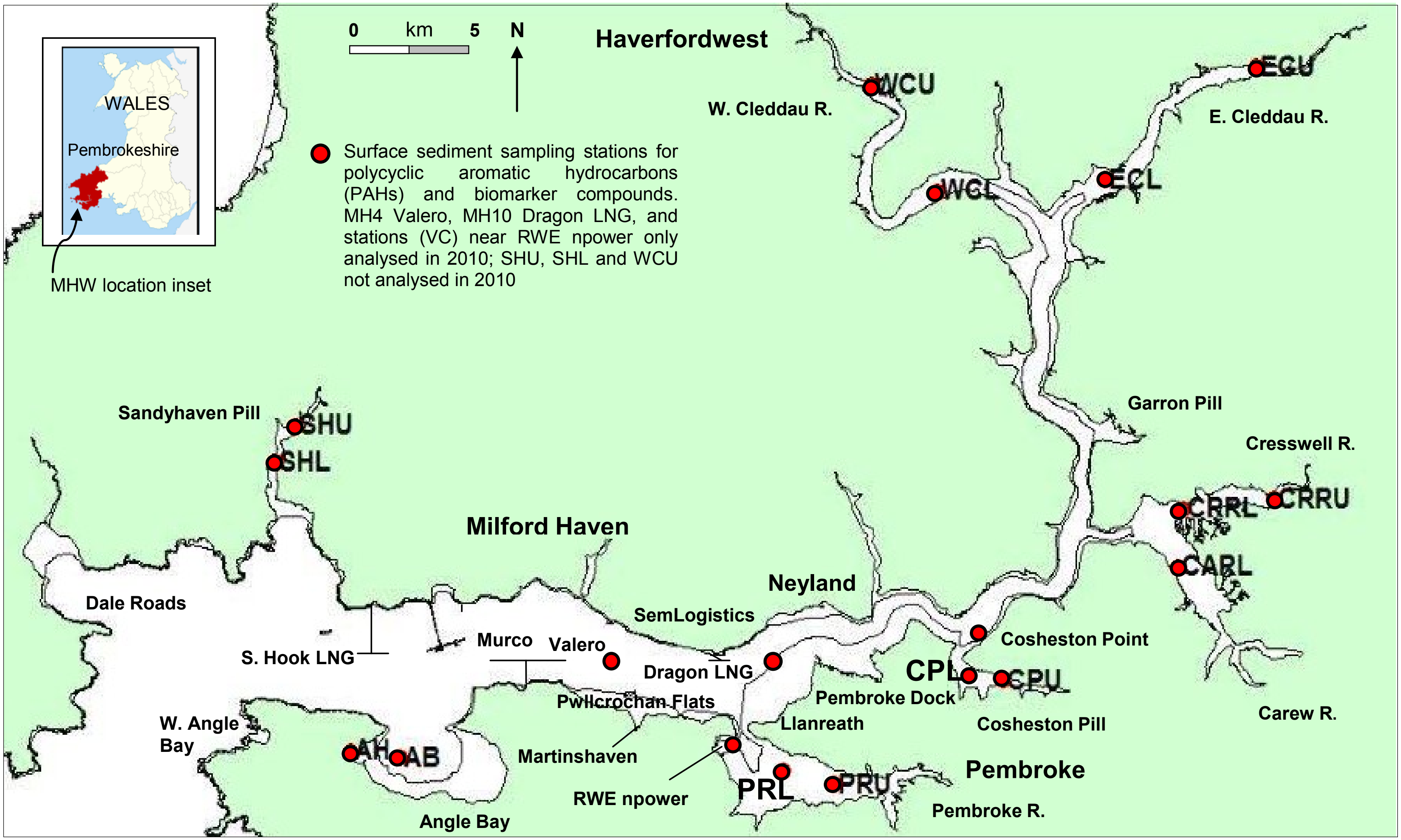
Figure 10 Shorelines affected by *El Omar* crude oil (after Little[37]), showing the uppermost extent of oiling in the estuary during 1988 (★= spill release site in December 1988; (●) = stranded oil reported in 1988)

Figure 11 Cross plot of PAH source ratios in sediments and biota between 1993 – 2012 (Yunker[19]; BA/[BA+C] vs. FL/[FL+PY]). Notes: MHWESG 1993 = pre-*Sea Empress* data; SEEEC 1996 = seven months post-*Sea Empress* data, with 5 lower estuarine sampling points showing petrogenic inputs; oval **A** = present study combining ERT 2010 and CCW 2012 EU Habitats data; oval **B** = CCW 2007 EU Habitats data; oval **C** = CEFAS 2001-2006 pre-dredging licence data; rectangle **D** = CEFAS 2008-2012 pre-dredging licence data; for labels see Table 1 and Fig. 1)

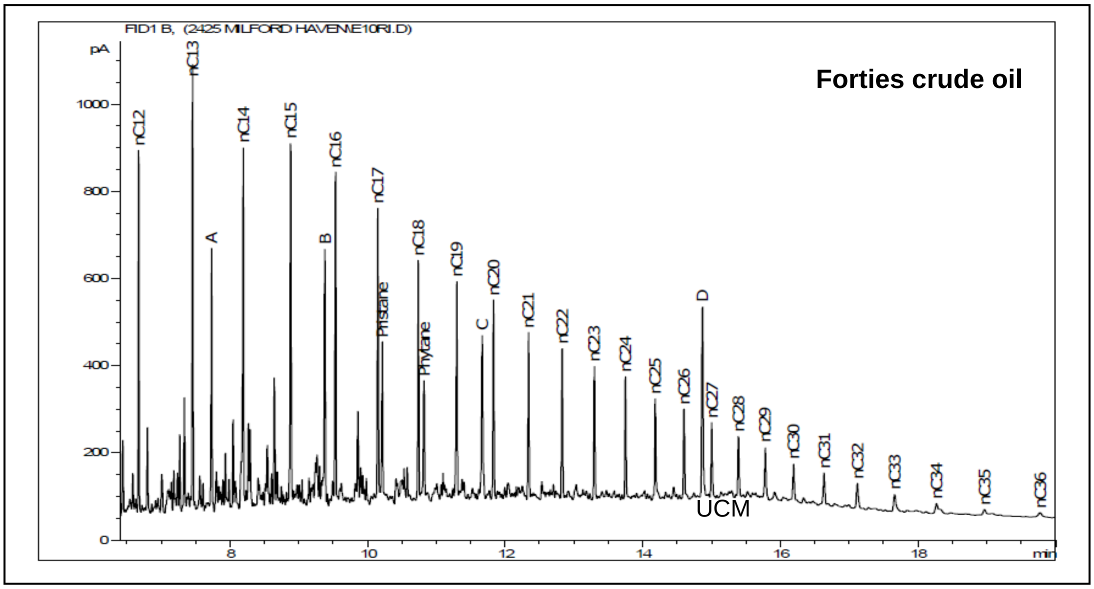
Figure 12 Cross plots of PAH source ratios in sediments and biota from various MHW and South Wales surveys superimposed on ERT 2010 data (●). Notes: cross-hatched ovals = CCW 2012; wavy ovals = CSEMP Cosheston Point 1999-2011; clear ovals = Defra air quality in Newport and Port Talbot 1999-2006; for labels see Table 1 and Fig. 1)

Figure 13 Cross plot of petrogenic PAH source ratios from CCW 2012 data (smaller oval) superimposed on ERT 2010 data (larger clear oval); ratios for reference samples SE Bunker, Iranian, Kuwait and Venezuelan crude oils, and RFA *Darkdale* are >1 and not shown in the plot (for labels see Table 1 and Fig. 1)

Figure 14 Map showing three areas (boxed) of probable and possible dredging or construction disturbance of sediments, visible in May 2012 in SPI survey at 37 out of a total of 559 stations in MHW. Two such examples of SPI are shown, one each from flood- and ebb-tide dominated areas. Also indicated are three further dredging areas that are fine-grained and do not show clearly visible disturbance in the SPI (Germano[41])



● Surface sediment sampling stations for polycyclic aromatic hydrocarbons (PAHs) and biomarker compounds. MH4 Valero, MH10 Dragon LNG, and stations (VC) near RWE npower only analysed in 2010; SHU, SHL and WCU not analysed in 2010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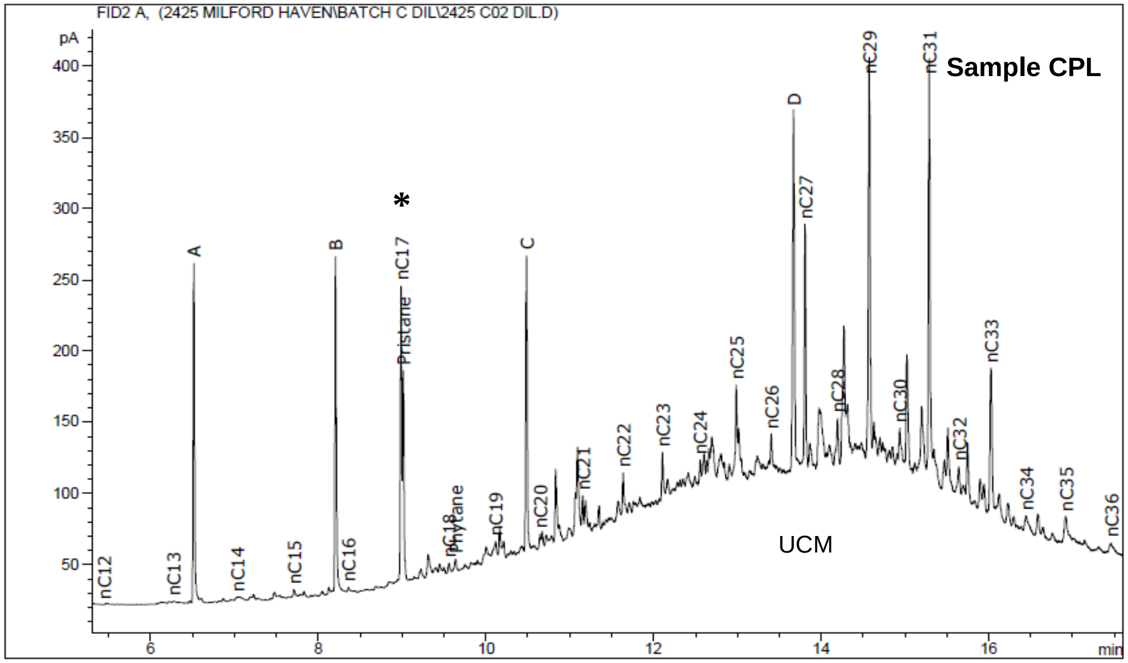
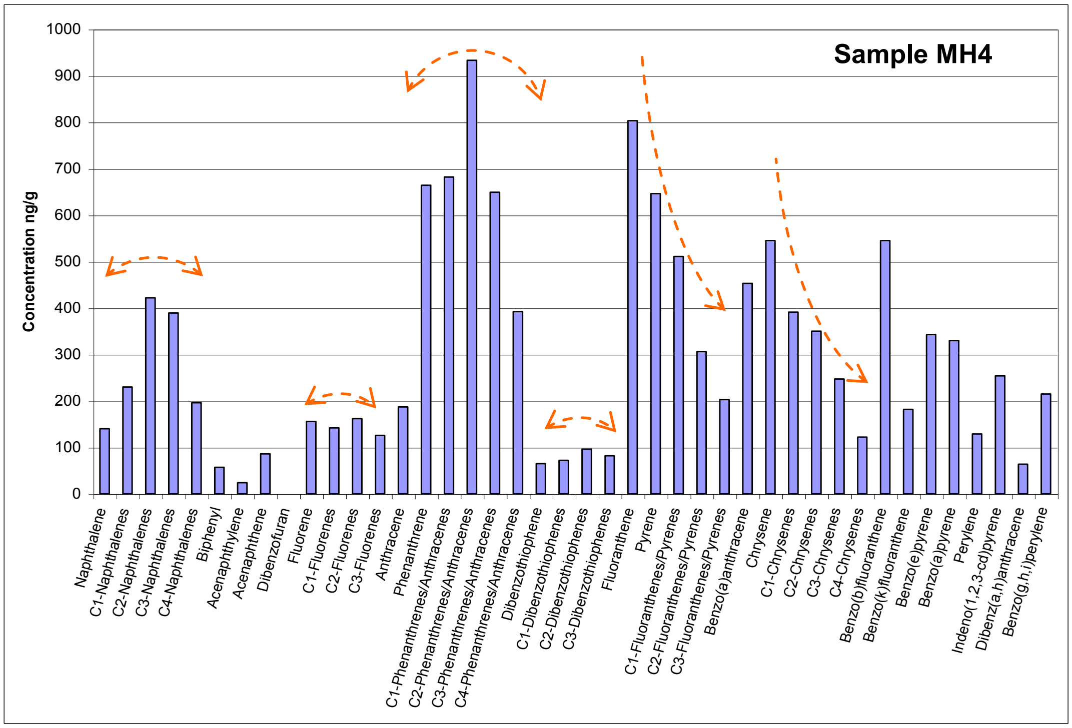
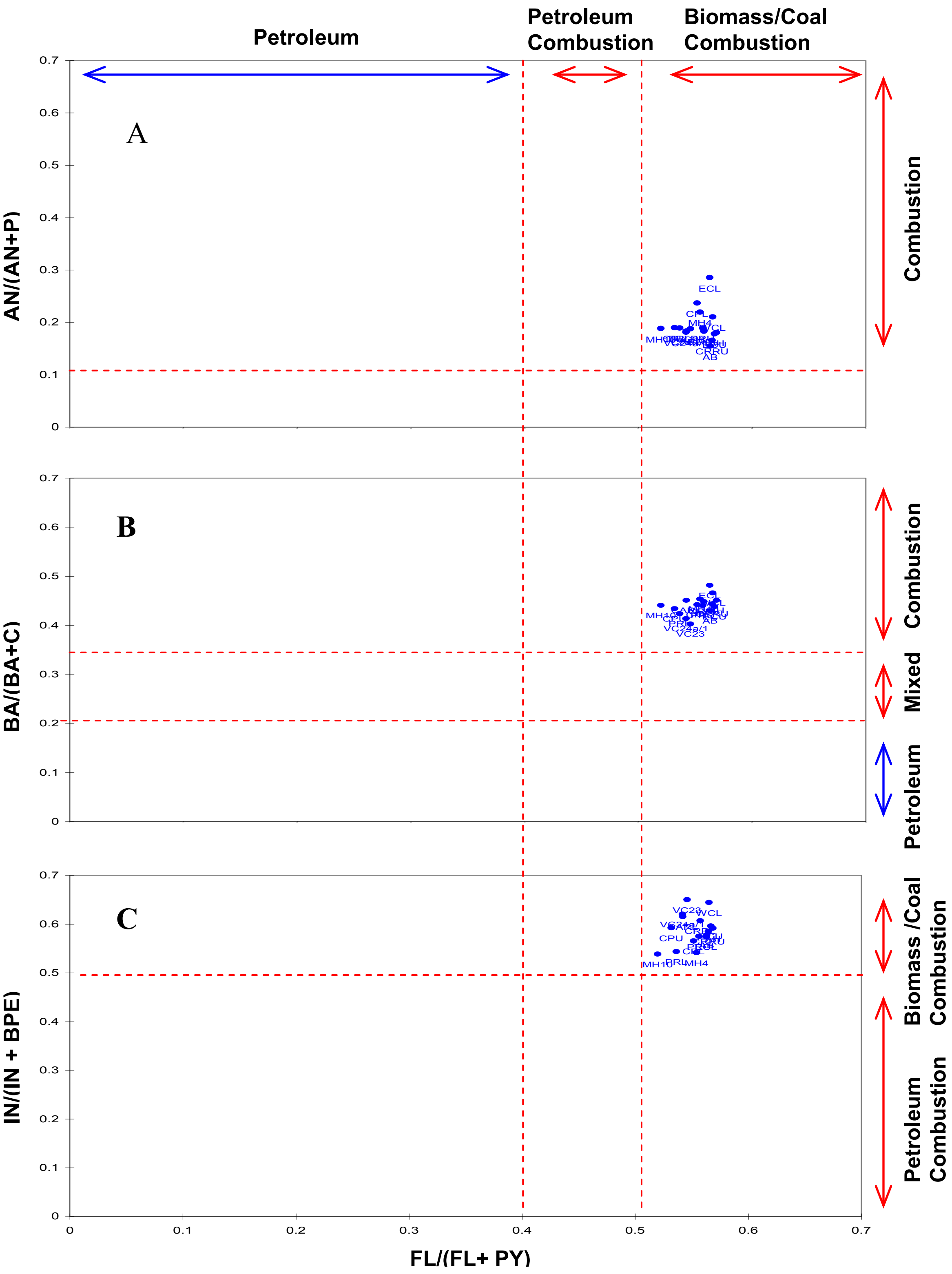
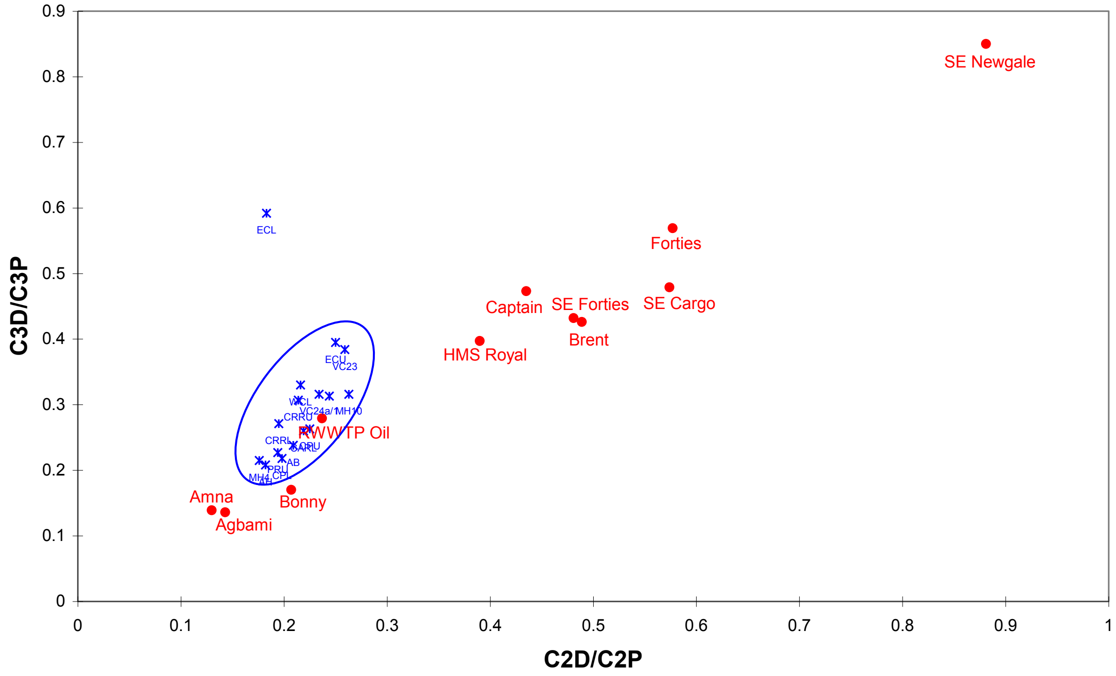
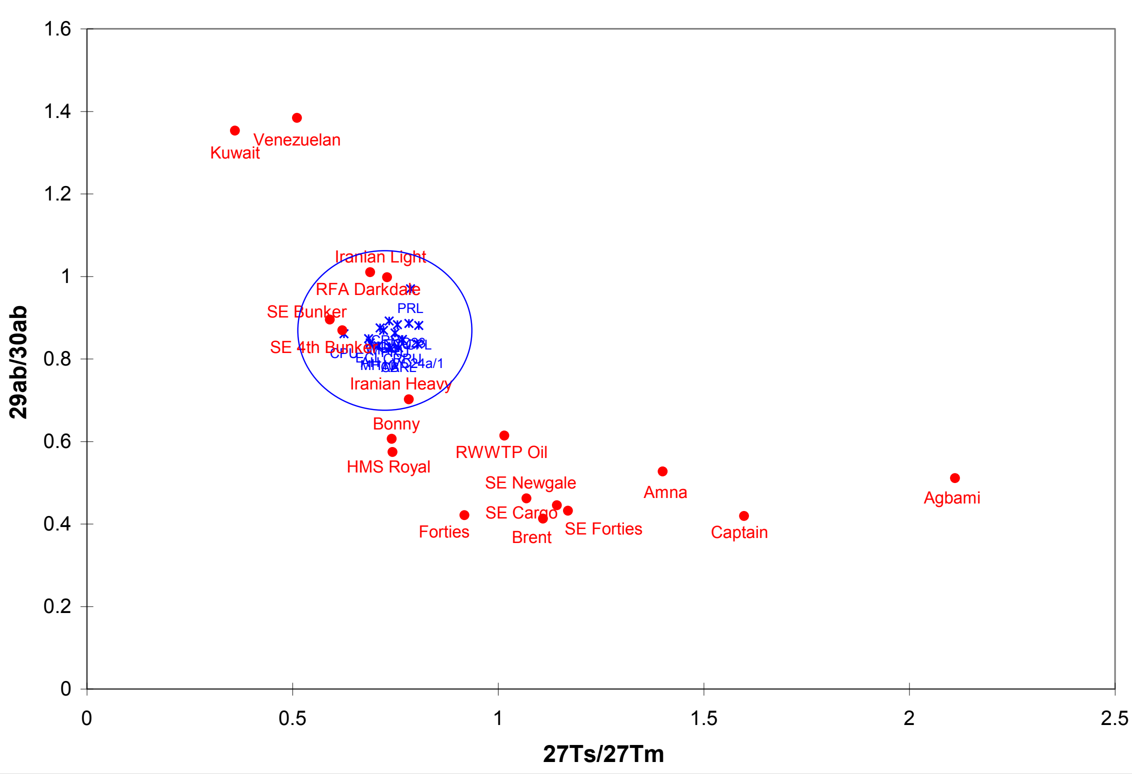
nC30
nC31
nC32
nC33
nC34
nC35
nC36
UCM
8
10
12
14
16
18
min

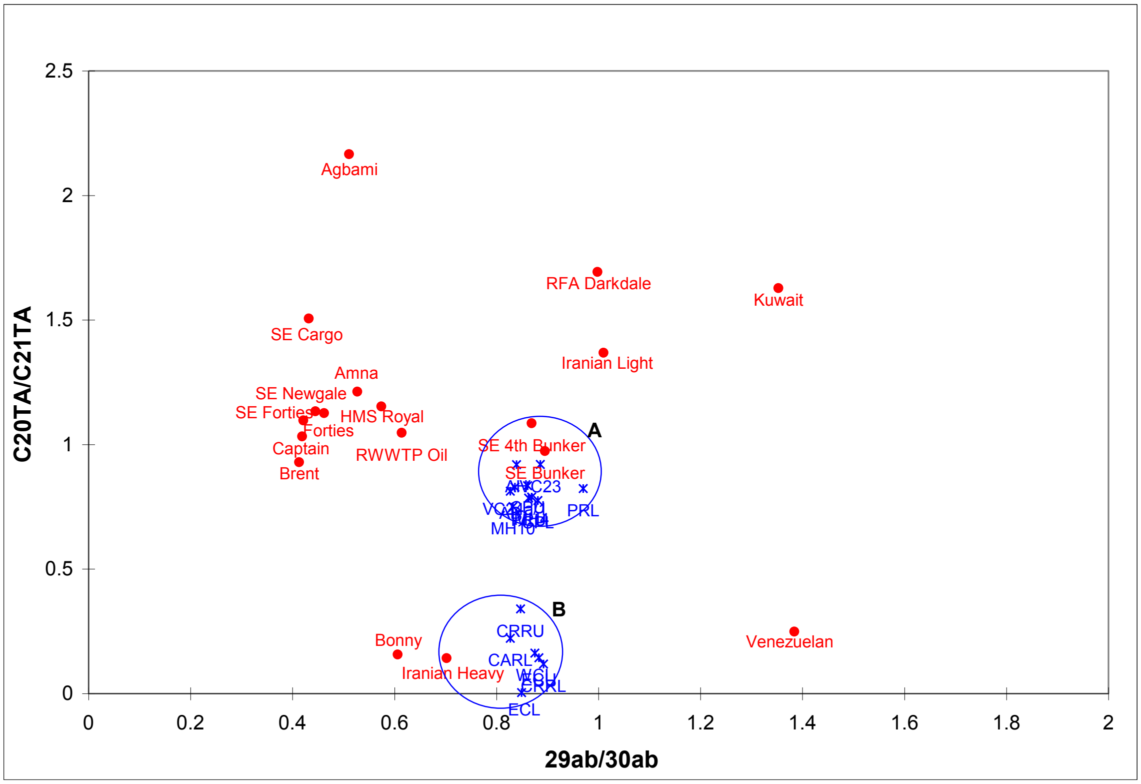

FID2 A, (2425 MILFORD HAVEN\BATCH C DIL\2425 C02 DIL.D)
pA
400
350
300
250
200
150
100
50
6
8
10
12
14
16
min
Sample CPL
nC12
nC13
A
nC14
nC15
B
nC16
*
nC17
Pristane
nC18
Phytane
nC19
C
nC20
nC21
nC22
nC23
nC24
nC25
nC26
D
nC27
nC28
nC29
nC30
nC31
nC32
nC33
nC34
nC35
nC36
UCM

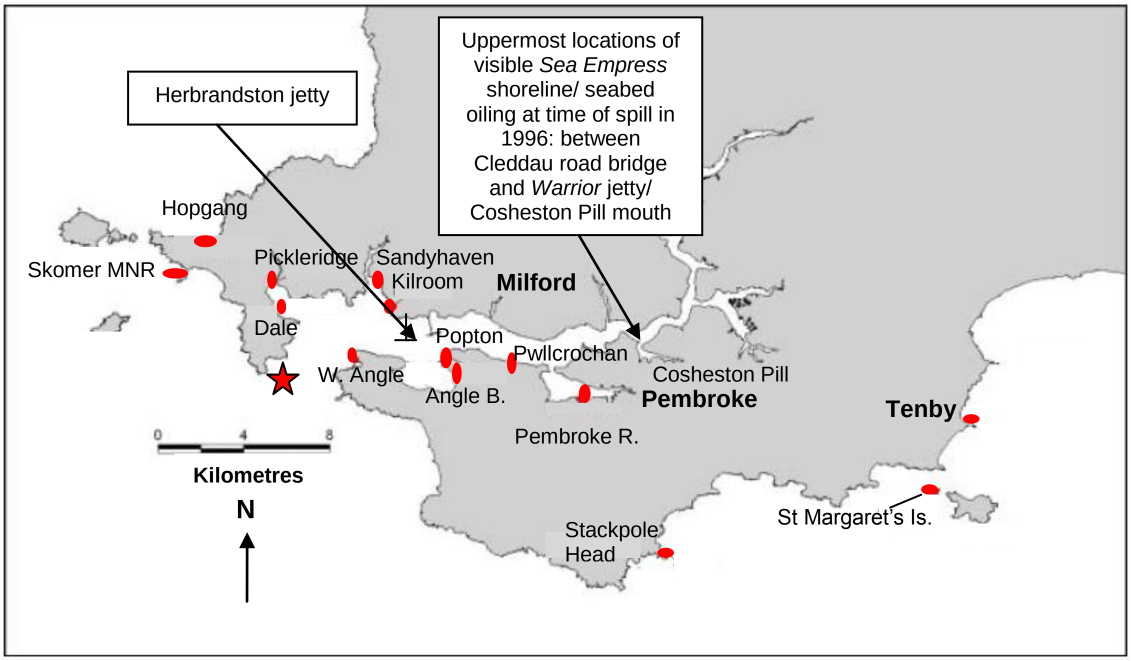

Sample MH4
Concentration ng/g
0
100
200
300
400
500
600
700
800
900
1000
Naphthalene
C1-Naphthalenes
C2-Naphthalenes
C3-Naphthalenes
C4-Naphthalenes
Biphenyl
Acenaphthylene
Acenaphthene
Dibenzofuran
Fluorene
C1-Fluorenes
C2-Fluorenes
C3-Fluorenes
Anthracene
Phenanthrene
C1-Phenanthrenes/Anthracenes
C2-Phenanthrenes/Anthracenes
C3-Phenanthrenes/Anthracenes
C4-Phenanthrenes/Anthracenes
Dibenzothiophene
C1-Dibenzothiophenes
C2-Dibenzothiophenes
C3-Dibenzothiophenes
Fluoranthene
Pyrene
C1-Fluoranthenes/Pyrenes
C2-Fluoranthenes/Pyrenes
C3-Fluoranthenes/Pyrenes
Benzo(a)anthracene
Chrysene
C1-Chrysenes
C2-Chrysenes
C3-Chrysenes
C4-Chrysenes
Benzo(b)fluoranthene
Benzo(k)fluoranthene
Benzo(e)pyrene
Benzo(a)pyrene
Perylene
Indeno(1,2,3-cd)pyrene
Dibenz(a,h)anthracene
Benzo(g,h,i)perylene

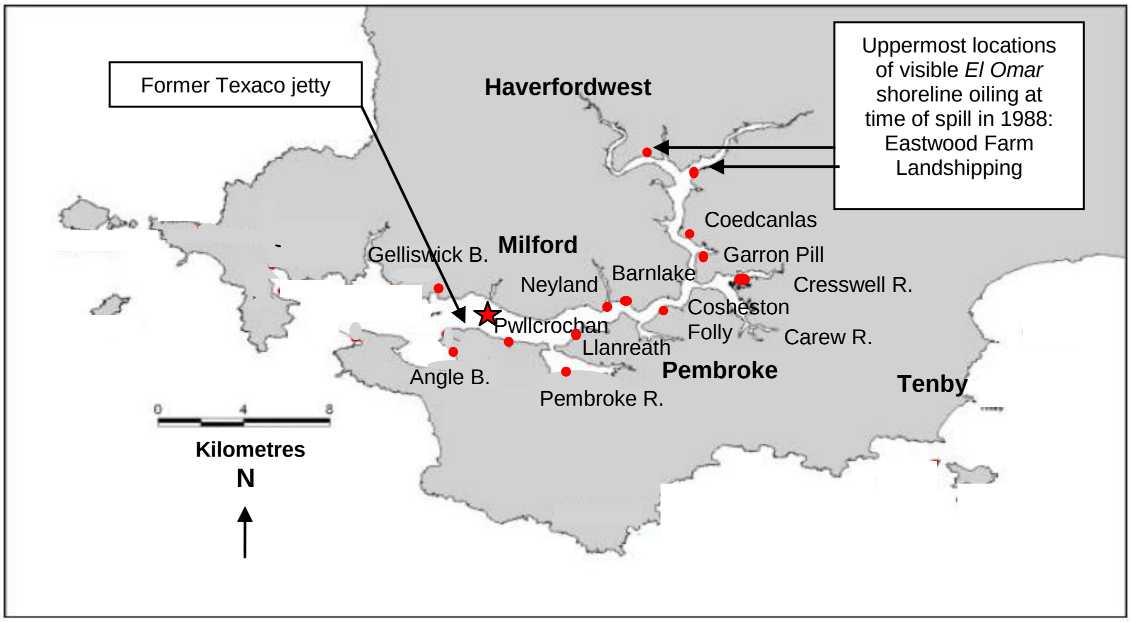

Petroleum
Petroleum Combustion
Biomass/Coal Combustion
A
AN/(AN+P)
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0
Combustion
ECL
CPL
MH4
CL
MH10
CRRU
AB
B
BA/(BA+C)
Combustion
Mixed
Petroleum
ECL
MH10
CPL
PRL
VC24a/1
VC23
AB
C
IN/(IN + BPE)
Biomass /Coal Combustion
Petroleum Combustion
VC23
WCL
VC24a/1
CPU
CRRU
CPL
MH10
PRL
MH4
0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
FL/(FL+ PY)

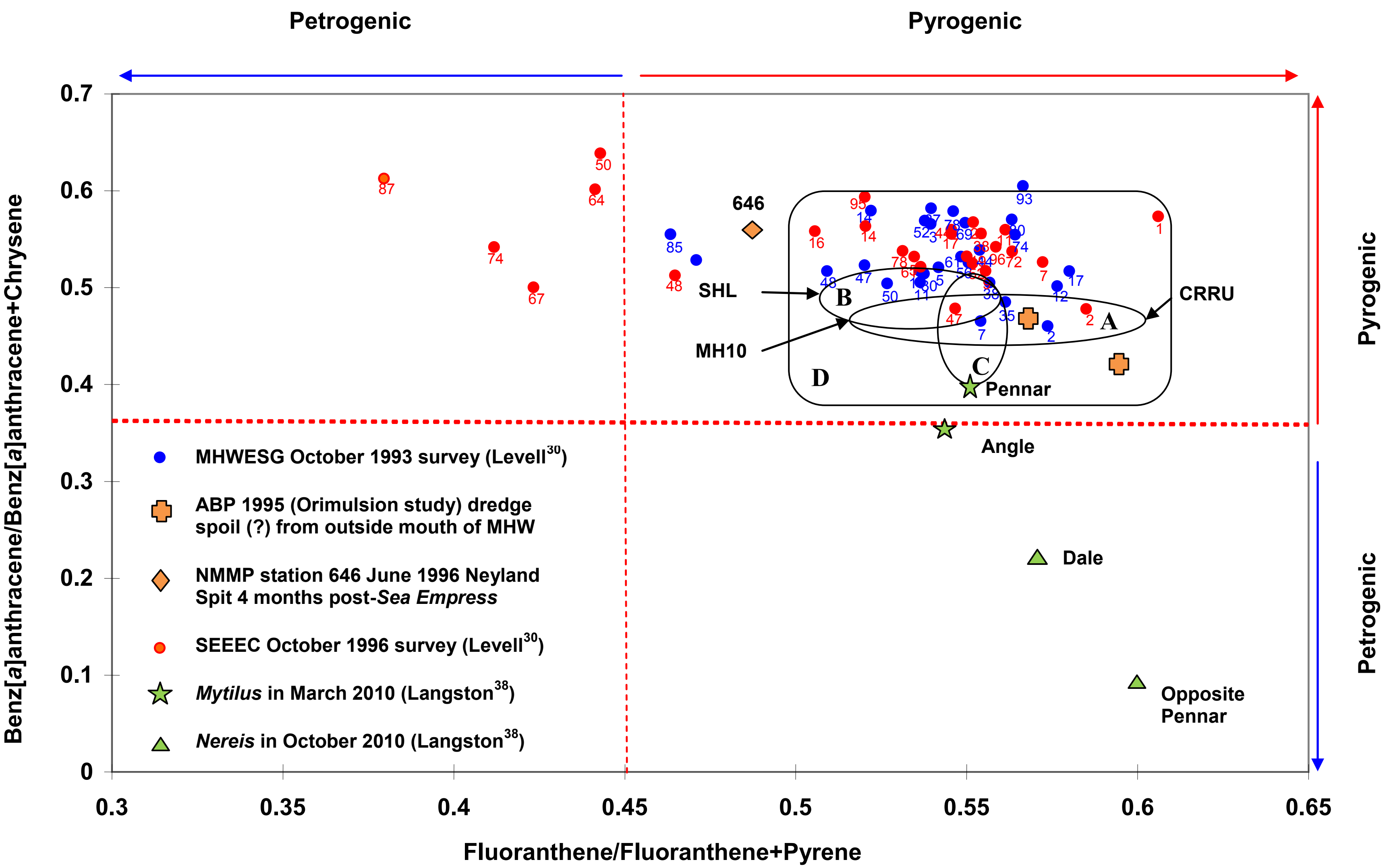

0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0
C3D/C3P
0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
0.8
0.9
1
C2D/C2P
SE Newgale
ECL
Forties
Captain
SE Forties
SE Cargo
Brent
HMS Royal
ECU
VC23
WCL
VC24a/1
MH10
CRRU
RWWTP Oil
CRRL
CRU
CARL
AB
PRU
MH4
CPL
AH
Amna
Bonny
Agbami

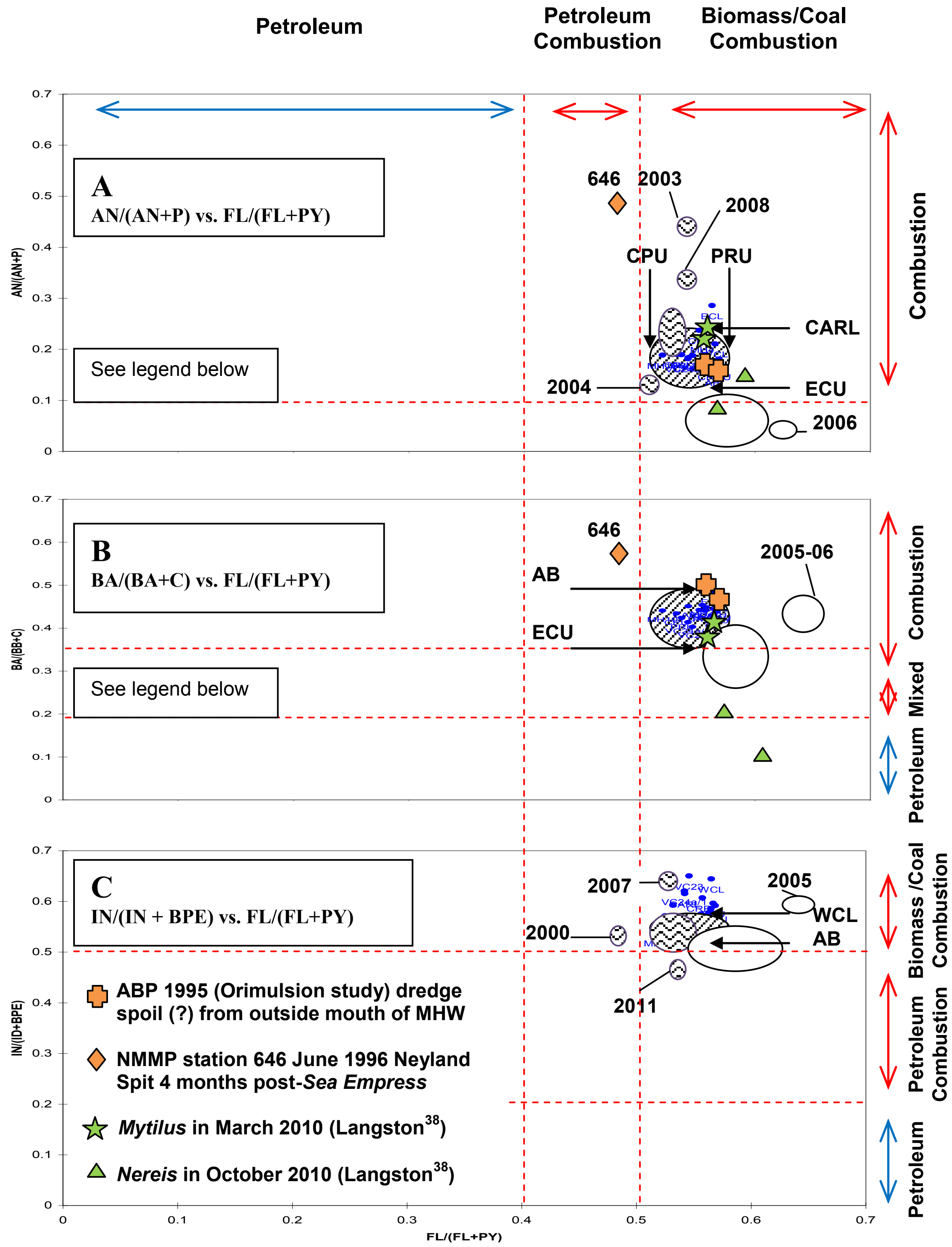

29ab/30ab
27Ts/27Tm
0
0.2
0.4
0.6
0.8
1
1.2
1.4
1.6
0
0.5
1
1.5
2
2.5
Kuwait
Venezuelan
Iranian Light
RFA Darkdale
SE Bunker
SE 4th Bunker
PRL
CPU
24a/1
Iranian Heavy
Bonny
HMS Royal
RWWTP Oil
SE Newgale
SE Cargo
Forties
Brent
SE Forties
Amna
Captain
Agbami

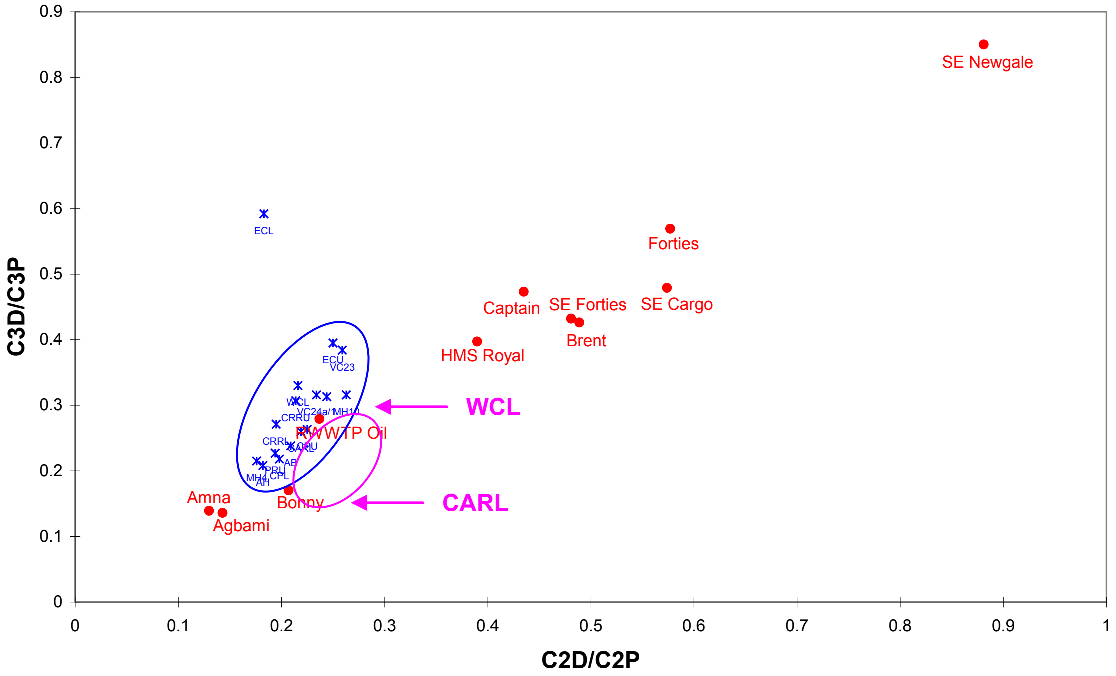

C20TA/C21TA
29ab/30ab
0
0.5
1
1.5
2
2.5
0
0.2
0.4
0.6
0.8
1
1.2
1.4
1.6
1.8
2
Agbami
RFA Darkdale
Kuwait
SE Cargo
Iranian Light
Amna
SE Newgale
SE Forties
HMS Royal
Forties
Captain
RWWTP Oil
Brent
SE 4th Bunker
SE Bunker
A
PRL
MH10
B
CRRU
Bonny
Venezuelan
CARL
Iranian Heavy
WCL
CRRL
ECL


Herbrandston jetty
Uppermost locations of visible *Sea Empress* shoreline/ seabed oiling at time of spill in 1996: between Cleddau road bridge and *Warrior* jetty/ Cosheston Pill mouth
Hopgang
Skomer MNR
Pickleridge
Sandyhaven
Kilroom
Milford
Dale
Popton
Pwllcrochan
W. Angle
Angle B.
Cosheston Pill
Pembroke
Tenby
Pembroke R.
0
4
8
Kilometres
N
Stackpole Head
St Margaret's Is.


Former Texaco jetty
Haverfordwest
Uppermost locations of visible El Omar shoreline oiling at time of spill in 1988: Eastwood Farm Landshipping
Coedcanlas
Garron Pill
Cresswell R.
Gelliswick B.
Milford
Neyland
Barnlake
Cosheston
Folly
Carew R.
Pwllcrochan
Llanreath
Pembroke
Tenby
Angle B.
Pembroke R.
0
4
8
Kilometres
N


Petrogenic
Pyrogenic
Pyrogenic
Petrogenic
Benz[a]anthracene/Benz[a]anthracene+Chrysene
Fluoranthene/Fluoranthene+Pyrene
0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
0.3
0.35
0.4
0.45
0.5
0.55
0.6
0.65
87
50
64
74
67
85
48
646
16
95
14
14
93
1
17
12
2
7
35
47
50
11
SHL
MH10
CRRU
A
B
C
D
Pennar
Angle
Dale
Opposite Pennar
MHWESG October 1993 survey (Levell30)
ABP 1995 (Orimulsion study) dredge spoil (?) from outside mouth of MHW
NMMP station 646 June 1996 Neyland Spit 4 months post-Sea Empress
SEEEC October 1996 survey (Levell30)
Mytilus in March 2010 (Langston38)
Nereis in October 2010 (Langston38)

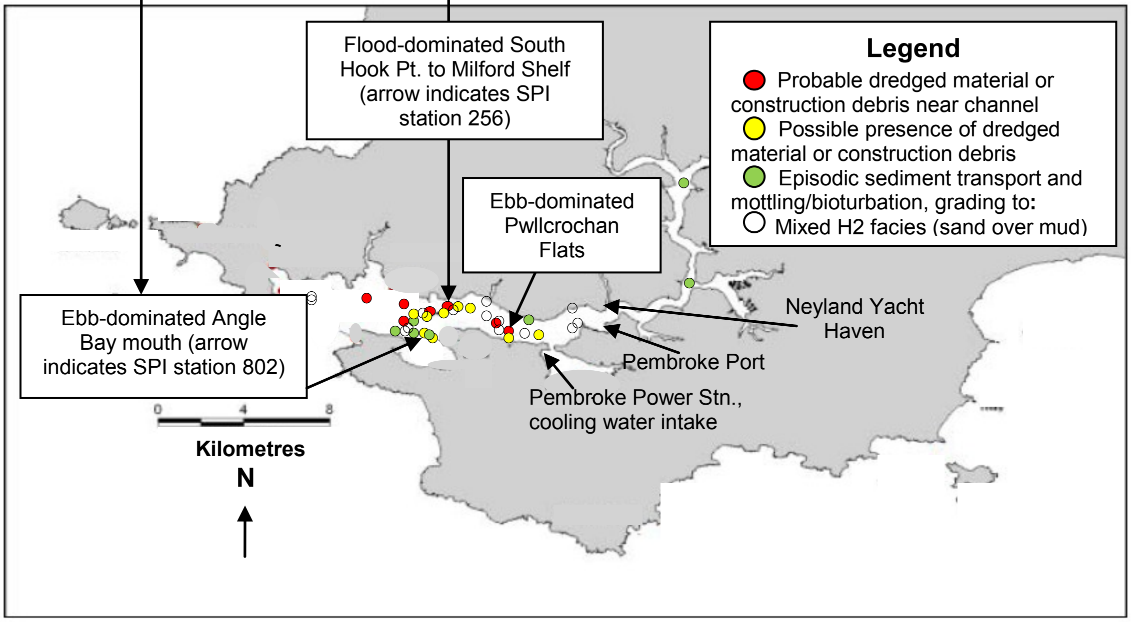

Petroleum
Petroleum Combustion
Biomass/Coal Combustion
A
AN/(AN+P) vs. FL/(FL+PY)
See legend below
AN/(AN+P)
646
2003
2008
CPU
PRU
CARL
2004
ECU
2006
Combustion
B
BA/(BA+C) vs. FL/(FL+PY)
See legend below
BA/(BB+C)
646
AB
2005-06
ECU
Combustion
Mixed
Petroleum
C
IN/(IN + BPE) vs. FL/(FL+PY)
IN/(ID+BPE)
2007
2005
WCL
AB
2000
2011
Biomass /Coal Combustion
Petroleum Combustion
Petroleum
ABP 1995 (Orimulsion study) dredge spoil (?) from outside mouth of MHW
NMMP station 646 June 1996 Neyland Spit 4 months post-Sea Empress
Mytilus in March 2010 (Langston38)
Nereis in October 2010 (Langston38)
0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
FL/(FL+PY)


0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0
C3D/C3P
SE Newgale
ECL
Forties
Captain
SE Forties
SE Cargo
Brent
HMS Royal
ECU
VC23
WCL
VC24a/1
MH10
CRRU
RWWTP Oil
CRRL
CPRU
CARL
AB
PRU
MH4
CPL
AH
WCL
Amna
Bonny
CARL
Agbami
0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
0.8
0.9
1
C2D/C2P

Sediment Profile Imagery (SPI) showing likelihood of dredging effects in mixed H2 facies (sand over chaotic/ mottled muds), and other features including episodic transport, ripple bedform asymmetry, abundant anemones, burrowing polychaetes, hermit crab)

SPI station 802
Mouth of Angle Bay
(N 51°41.5341'; W 5°04.1845'; water depth 7.6 m; prism penetration depth 8.5 cm; apparent redox potential discontinuity 2.6 cm)

SPI station 256
Offshore Hakin Pt.
(N 51°42.3757'; W 5°02.8980'; water depth 6.2 m; prism penetration depth 12.5 cm; apparent redox potential discontinuity 2.4 cm)



Legend
🔴 Probable dredged material or construction debris near channel
🟡 Possible presence of dredged material or construction debris
🟢 Episodic sediment transport and mottling/bioturbation, grading to**:**
○ Mixed H2 facies (sand over mud)