

Theme Session on Oil Spills in Marine Ecosystems: Impacts and Remediation (S)

ICES CM 2005/S:01

Opportunities for at-sea response and beach clean-up to reduce the impact of oil spills: examples from the “Sea Empress” incident

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The tanker “Sea Empress” ran aground at the entrance to Milford Haven, west Wales in 1996, spilling 72 000 tonnes of Forties blend crude oil and 480 tonnes of heavy fuel oil. This led to contamination of 200 km of coastline. The coastline around south-west Wales is of exceptional conservation interest, and the area also supports a diverse fishery with extensive shellfish beds in some of the estuarine areas. In order to reduce the quantity of oil reaching the beaches and responding to opportunity, a vigorous aerial dispersant spraying operation was mounted, alongside other options such as at-sea recovery. Despite the success of the spraying operation, over 100 separate sites required cleaning. The coastline has a wide range of different types of shore, often in close proximity, such as sandy shores with high amenity use; rocky, cobble, and shingle beaches with cliffs, and beaches with difficult access. It is also very rugged with many remote coves which can hold oil and release it later to recontaminate already cleaned areas. The majority of the sites were environmentally sensitive. Initially, priority was given to amenity beaches so that they could be available for the Easter Holiday period. Cleaning of the remaining sites was developed on an individual basis so as to minimize long-term damage. Overall, the aim was to reach the “least worst” outcome from the spill, often described as net environmental benefit analysis.

Keywords: oil spills, at-sea response, clean-up, net environmental benefit, “Sea Empress”.

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How to model the oil combating technologies and their impacts on ecosystem: a Bayesian networks application in the Baltic Sea

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Oil spills from ship grounding and collision are increasingly feared as oil transports have increased. Mitigation of the negative consequences at the biological and economic level is a difficult resource-consuming task where the effectiveness of counter-measures is dependent on technological factors and environmental conditions. Such measures are, for instance, sealing of cracks in the tanker hull, limiting the use of the load

carrying capacity of tankers, use of dispersants, use of oil combating vessels with certain deployment time and collection capacity.

To assess the effectiveness of oil combating technologies, implemented singly or jointly in the case of oil spill, entails probabilistic modelling of their influences with respect to consequences. The paper introduces a Bayesian Network that can be used for analysing the mitigation options under user-defined scenarios, where the scenarios are defined in terms of technological performance and weather conditions. All estimates are probabilistic, i.e., they enable the modelling of improvement in the quality of the knowledge. The consequences are assessed with respect to the change of state of the population of birds, herring, seals, and benthos, including also long-term biological effects. Intermediate consequences are estimated as a function of the amount of oil in the water and the amount of polluted shore length.

We present some selected scenarios to demonstrate the consequence analysis performed by the Bayesian Network model. The baseline /reference scenario is defined to reflect the current oil combating effect in general environmental conditions in the Baltic Sea. Probabilistic decision analysis enables the estimation of value-of-information (focusing of additional research) and value-of-control (impact of additional control tools) in planning oil spills management.

Keywords: oil combating, ecosystem impacts, Bayesian decision analysis, environmental risk analysis.

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Monitoring the “Prestige” oil spill impacts on the northern Iberian shelf ecosystem

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The aim of this study was to assess the possible effects of the “Prestige” oil spill (POS) through different shelf communities and their trophic cascade of those effects to high trophic levels. No significant correlations between tar aggregates and species richness, biomass, and diversity of benthic communities were found. Selected key components of the continental shelf benthic and demersal communities were monitored to identify the possible ecological effects of the oil. This work includes the first results regarding changes in abundance, distribution, and food habits of hake (*Merluccius merluccius*), four-spot megrim (*Lepidorhombus boscii*), Norway lobster (*Nephrops norvegicus*), and Pandalid

shrimp (*Plesionika heterocarpus*) populations of Galician and Cantabrian Sea shelves following the POS. Significant reductions in the abundance of *Nephrops norvegicus*, *Plesionika heterocarpus*, and four-spot megrim were detected in the POS maximum impact area. No significant effects on the abundance or distribution of hake juveniles were detected even though the tar aggregates were bound by the same oceanographic drift events as the hake recruits in different water column layers of the Cantabrian Sea. Feeding patterns of the four species analysed do not present apparent modifications that can be related to the POS.

Keywords: "Prestige" oil spill, food web, hake, megrim, *Nephrops*, tar aggregates.

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Effects of bioremediation on mutagenicity of fuel oil coming from the "Prestige" spill: *in situ* experiments in Sorrizo's Beach (NW Spain)

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The last large black tide in European Atlantic waters happened in northwestern Spain when the "Prestige" sank in November 2002 and contaminated the Galician coastline with 60 000 t of fuel oil. This kind of fuel contains appreciable quantities of polycyclic aromatic hydrocarbons (PAHs). Given that many PAHs are known mutagens and carcinogens, its occurrence in the environment is of great concern. The bioremediation is probably the best alternative to release these compounds. However, this process would lead to higher mobility of otherwise insoluble components of fuel oil or increase the concentrations of intermediate metabolites with mutagenic activity.

Because of this, in the study we evaluated any change in the mutagenicity of the bioremediated fuel oil in Sorrizo's Beach, an area affected by the "Prestige" oil spill, using the *Salmonella* mutagenicity test. The fuel oil was applied to tiles of granite in the intertidal shoreline and submitted to four bioremediation processes: applications of fertilizer, addition of biodiesel, treatment with indigenous and with alloctons microorganisms. The tiles submitted to different treatments were sampled and oil extraction of each one was made to evaluate their mutagenic potential. Positive results were obtained with all the samples when *Salmonella typhimurium* TA98 was used in the assays. Under the conditions tested, our results indicate that along the period of study (2 months), the bioremediation strategies were not effective in reducing the mutagenic activity detected in the fuel oil coming from the "Prestige".

Keywords: bioremediation, Ames Salmonella assay, fuel oil spills.

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Seasonal variability of predator fish trophic levels before and after the "Prestige" oil spill

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Whether or not changes have occurred on the trophic levels of fish related with the "Prestige" Oil Spill (POS) still has not been investigated. Three years after the POS we analyze this matter using data on stomach contents corresponding to 10 demersal fish species of the continental shelf of Northwest of Spain.

The data analyzed come from surveys carried out in the springs and autumns of 1997 and 2002 (pre-spill), and in the springs and autumns of 2003 and 2004 (post-spill). The trophic levels of each species are estimated using the different proportions of preys (considering their length ranges) in the predators diet composition found in each survey.

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Biomarker responses in demersal fish from the northern Iberian shelf: Results one year after the "Prestige" oil spill

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Because to the magnitude and wide dispersion of the POS, a multidisciplinary project was developed to establish its impact on the ecosystems and fishery resources along the northern Spanish shelf. It must be pointed that, until the "Prestige" sank, no studies using biomarkers in fish species had been made in the northern Spanish shelf. Liver tissues of *Lepidorhombus boscii* and *Callionymus lyra* were sampled along the Galician-Cantabrian shelf six months (April 2003) and one year (October 2003) after the "Prestige" oil spill (POS). 7-ethoxyresorufin-O-deethylase, glutathione S-transferase, glutathione-reductase, and catalase activities were determined in both species, and an evaluation of genotoxic damage was made. Biomarker responses reflected the spatial distribution pattern of the tar aggregates resulting from the POS along the shelf. In April 2003, a significant correlation ($p < 0.05$) was found between the EROD activity measured in *L. boscii* and the fuel deposits and higher values were systematically observed in Finisterre. One year after the POS happened,

the results showed a higher exposure to organic pollutants along the inner shelf but not at the middle and external shelf environments. Although the results may indicate a possible causal link POS and the marine current processes, the lack of previous data together with the existence of chronic pollution in certain zones of the inner shelf, mean that the biological effects observed cannot be attributed exclusively to the POS. However, they do provide an overall view of the situation prevailing along the north Spanish shelf during this period.

Keywords: biomarkers, *Callionymus lyra*, Spanish continental shelf, *Lepidorhombus boscii*, "Prestige" oil spill, sublethal effects.

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Chronic exposure to polynuclear aromatic hydrocarbons in natal habitats leads to decreased productivity and fitness in pink salmon populations

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The immediate and delayed effects of embryonic exposure to low levels of polynuclear aromatic hydrocarbons (PAHs) reduce survival to maturity by 50% in exposed pink salmon populations, indicating that chronically exposed populations should rapidly decline to extinction. However, density dependence may prevent or delay extinction. This report measures the effects of chronic exposure on a simulated pink salmon population. The simulation uses empirically derived survival functions based on 70 years of observations of a single population. The survival functions are combined with the effects of embryonic exposure to PAHs on survival to determine how chronic exposure affects population productivity (median number of returns), fitness (median returns-per-spawner), and the probability of extinction over 35 generations. The PAH effects were observed among fish rearing in the same watershed as the modeled population. The resulting models predict that at low levels of exposure, density dependence compensates for reduced productivity, buffering the population against extinction. However, as toxicity increases, random environmental variation overcomes this buffering effect and extinction probability increases. For example, exposing 100% of the population to aqueous PAH concentrations of 18 parts-per-billion leads to an 80% decrease in population productivity and an 11% probability of extinction within 35 generations. Increasing the relative toxicity of the exposure by 60% results in a 100% probability of extinction. These data demonstrate that chronic contamination of natal fish habitats at PAH concentrations near statutory limits can significantly reduce population productivity and stability.

Keywords: oil exposure, population effects, density dependence, salmon.

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"Exxon Valdez" oil spill: PAH persistence in intertidal sediments, bioavailability, and long-term effects

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In 2001, 12 years after the "Exxon Valdez" oil spill, surprising quantities of oil were found in over half the beaches surveyed. Approximately 100 formerly impacted beaches were resurveyed for the presence of oil (over 9000 assessment pits). Liquid crude oil was found in some pits; all subsurface oil could still be fingerprinted to "Exxon Valdez" oil. Subsurface oil was most abundant at the mid-tide level, but extended down to the zero tide level, and well into the biological zone of mussels and clams. PAH bioavailability is limited to species that live or forage in the intertidal zone: mussels, clams, Harlequin ducks, and sea otters show evidence of exposure and harm more than 10 years after the spill. Population recovery of sea otters is a function of scale: total numbers indicate recovery, yet some bays with persistent oil do not support use by sea otters. While the exposure was relatively universal in Prince William Sound at the time of the spill, present day exposures are very site specific and limited in space to specific patches of lingering oil.

Keywords: "Exxon Valdez", oil, persistence, PAH, mussels, sea otters, clams, intertidal sediments.

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Marine oil spill bioremediation: field studies for development of operational spill response strategies

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Microbial degradation is a principal process mediating the elimination of petroleum hydrocarbons spilled in the marine environment. In recent years, a number of bioremediation strategies have been proposed. However, wide acceptance and use of bioremediation strategies by the oil spill response community has been limited by conflicting results observed in efficacy studies associated with various spill response operations. To address this issue, largely attributed to differences in treatment

protocols and heterogeneity within the natural environment, we conducted a series of controlled oil spill experiments. As bioaugmentation in the open environment was found to be ineffective, the focus of our studies was on biostimulation protocols. These were based on the alteration of habitat quality to stimulate the growth of indigenous oil degraders by enhancement of nutrient and oxygen levels, plant growth, and/or physical dispersion processes. Monitoring programs were developed to quantify intrinsic rates of oil loss and degradation, demonstrate treatment efficiency (e.g., alteration of microbial structure and function) and identification of habitat recovery. As a direct result of these studies, new operational spill response strategies have been proposed for marine oil spill bioremediation.

Keywords: oil spills, bioremediation, biodegradation, phytoremediation, natural attenuation, oil-mineral aggregates, flocs, habitat recovery.

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PAH levels and evolution in water, sediments and biota after the “Prestige” oil spill

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On the 13 November 2002, the single-hulled, 26-year-old tanker “Prestige” started leaking part of the 77 000 tonnes of heavy fuel oil that she was carrying. Due to the towing of the tanker along the coastal water and then out to sea until it finally broke and sank, it was spilling its cargo and slicks in successive waves that reached virtually the whole of Spanish Northern coastline, and even got to the French coast.

The Instituto Español de Oceanografía (IEO) was one of the Spanish institutions involved in the assessment of this impact, concentrating its main efforts in the platform area.

From December 2002, just 15 days after the wreck, six sampling surveys were developed in the area affected by the fuel in order to collect water and sediment samples and measure the hydrocarbon content. The data available at present covers the period from December 2002 to February 2005.

Wild mussels were also assessed as a “sentinel organism” and samples from most of the forty sites along the Spanish coast, usually studied in the National Monitoring Programme, have been collected every three months from February 2003 to date. Besides, different species of commercial molluscs, crustaceans and echinoderms were also analysed for PAHs.

Keywords: spill, PAHs, hydrocarbons, sediment, water, biota.

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Fisheries and “Prestige”. Review and update of the studies on the effects of the “Prestige” oil spill

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Most oil spills have been in the coastal zone; if they have taken place on the continental shelf, no industrial fishery was affected. In this case, the oil spill stretched along the whole continental shelf included in ICES Divisions VIIIc and IXa, affecting the majority of the pelagic and demersal industrial fisheries. An update of the studies on the effects of the “Prestige” oil spill on industrial fisheries developed in the zone and the main commercial species exploited by them, is presented. Until now, it has only been possible to analyze the information from the fisheries until 2003, the year of the maximum impact of the spill. This could have produced a distorted image of the effects of the spill. A compilation and update of the information until year 2004 is made, describing and analyzing the oil spill consequences in the fishing effort, catch composition, length distributions, and exploitation pattern of the main industrial fisheries.

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Use of biological life history, genetic, and vulnerability information to optimize the repertoire of oil combating technologies

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There are two decision-orientated issues related to the risk of a large oil spill in the Baltic Sea requiring scientific analysis. First of all, 1) how do we justify the requirements for substantial investments to prevent ecosystem impacts prior to accidents? Secondly, when an accident has happened, 2) how do we allocate the available oil combating resources to minimize the harm to the ecosystem? We demonstrate that there is a need to deal with these two decisions separately in a multidisciplinary context. This need is based on the

combined effects of biological characteristics of the populations in risk and on the technical possibilities to restrict impacts of an oil accident.

There are 3 factors which influence both decisions: 1) “Vulnerability of the population”, 2) “Uniqueness of the population (genetic specification of the population to the given environment)”, and 3) “Sustainability/regeneration potential of the population”. In addition, the 4) “Probability of an accident” is fundamental for the decisions regarding investments aimed at decreasing potential ecosystem tribulations. In the decision-making after the accident, 5) “Ability to protect the population by the available combating technology” is a key element.

The aim of this paper is to link the technical features of oil accident risk analysis to the ecosystem aspects of the decisions. We demonstrate that even though the technical features may dominate the quantitative side of risk analysis where direct probabilistic estimates are available, the ecosystem part (valuation) of the analysis seems to be the dominating part of the final decision-making.

Keywords: oil spill combating, decision analysis, genetic differences, ecosystem impacts.

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Assessing the long-term impact of oil spills: an examination of recent incidents

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Following major oil spill incidents there is a considerable focus on environmental impact assessment, particularly in the short term. These can arise both as a result of toxic impacts (toxicity and bioaccumulation) and physical impacts (smothering and sediment contamination). There may also be impacts as a result of remedial activities, for instance to sand-dune systems caused by heavy vehicle traffic. Different ecosystems also have varying recovery rates. Long-term impacts can be more difficult to assess, particularly against a background of natural variability and change which would occur in the absence of a spill. We plan to investigate the impact assessments made following a number of recent incidents (“Braer”, “Sea Empress”, “Erika”, “Prestige”, and “Tricolor”) and to try to assess whether the current framework of environmental risk assessment and toxicology is adequate to address the issues of long-term impacts of oil spills.

Keywords: oil spills, long-term impacts, “Braer”, “Sea Empress”, “Erika”, “Prestige”, “Tricolor”.

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Assessing the impact of oil spillages on plankton using the Continuous Plankton Recorder (CPR) survey

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On the 19 November 2002, the oil tanker “Prestige” sank and discharged 64 000 tonnes of fuel oil, approximately 230 km offshore North-western Spain (Galicia). The immediate effects of the spillage on higher trophic levels such as sea birds, fish, and cetaceans were noticeable, but the impacts on lower trophic levels such as phytoplankton and zooplankton are not well documented. The Continuous Plankton Recorder (CPR) survey provides multi-decadal information on plankton and is one of the longest marine plankton time-series. This survey has collected data from off the Galician coast since 1958, allowing a comparison between pre- and post-spill plankton communities. Here we use CPR data collected off the Galician coast to investigate changes in the abundance, diversity, and community structure of plankton. By comparison with pre-spill samples, we found there was an immediate decline in plankton followed by an increase in an index of chlorophyll two months after the spill, and an increase in copepods two months after this. There was thus no longer-term (over several months) decline in abundance, diversity, or change in plankton community structure, although there appeared to be a short-term immediate impact of the “Prestige” oil spill.

Keywords: “Prestige”, oil spill, plankton, Continuous Plankton Recorder, impact.

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Enhanced biodegradation of the “Prestige” fuel oil: laboratory and field observations

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Petroleum biodegradation by micro-organisms plays a dominant role in the later stages of weathering and the eventual elimination of oil from the marine environment, to the point that attempts have been made to stimulate natural biodegradation by the development of the so-called bioremediation techniques. An early assessment of the effects of biodegradation on the composition of the spilled oil will be useful not only for the feasibility studies regarding the application of these techniques but also for providing monitoring indicators of the natural

evolution of the spill, which will be particularly valuable for the source recognition of oil samples collected a certain time after the incident. The particular characteristics of the "Prestige" oil residue, devoid of the more labile fractions (b.p. < 300°C) and with high contents of aromatic hydrocarbons (~ 50%) and resins and asphaltenes (~ 30%) advocate for an assessment of the biodegradation process to better understand the ultimate fate of the stranded heavy oil. A laboratory assay was performed to provide preliminary information on the potential biodegradability of the heavy oil, using two microbial consortia and hydrophilic and oleophilic nitrogen-phosphorus fertilizers (S200). S200 strongly increased the extent of biodegradation, especially of recalcitrant compounds. A subsequent field assay showed an enhanced biodegradation of both the aliphatic and aromatic fractions. A number of molecular indices were defined for a further insight into the understanding of some biodegradation pathways and the surveillance of the oil spill.

Keywords: "Prestige" oil spill, heavy fuel oil, microbial consortia, biodegradation, oleophilic fertilizer, molecular markers.

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Crude oil bioremediation field experiment at a shore in the Sea of Okhotsk in Hokkaido, Japan

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Recently, some large-scale offshore oil fields have been constructed and operated around Sakhalin, Russia. Although any severe oil spill from these facilities has never occurred, the coastal areas of Hokkaido, Japan would be damaged in case, because plenty of Sakhalin crude oil is being shipped through the Sea of Okhotsk. Although bioremediation has been investigated as an alternative tool for spilled oil clean-up at shores, microbial activity in cold marine environments is expected to be low. In addition, since only few field experiments of crude oil bioremediation have been implemented at shores in Japan, little is known about its efficacy and safety. We conducted an experimental crude oil bioremediation at a sandy beach in Hokkaido to evaluate the effect of the exogenous macronutrients (fertilizers) addition for stimulating microbial degradation of crude oil. Artificial mixtures of Arabian Light and Sakhalin crude oils and the sand taken from the experimental site were wrapped in polyester net envelopes and they were buried in the sand filling in stainless cages placed at the intertidal zone. Slow release nitrogen and phosphorus synthetic fertilizer granules were added to the oil-sand mixtures to stimulate indigenous oil-degrading bacteria, while some ones were

unfertilized controls. The oil-sand mixtures were periodically sampled and the changes in some hydrocarbons in the residual oils were monitored. We verified an apparent effect by exogenous fertilizer addition in stimulating the degradation of some hydrocarbons, but some unknown aliphatic hydrocarbons in Sakhalin crude oil were found to be recalcitrant.

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ICES CM 2005/S:19

Oil spill monitoring: analysis of similarities and differences in approaches and methodologies

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Monitoring of ecological impacts is generally set up in the wake of each major oil spill. However, the studies carried out in such context are different from one country to another. In fact, comparing what was monitored from one oil spill to another, it appears that for similar coastlines and pollutants, the material (communities or species targeted) and the methods are not systematically identical. These differences can be explained by various parameters such as the source and modalities of funding, the coordination structure, the extent of knowledge, the interest for such or such environmental community, the availability of research teams, or logically the type of oil. Moreover, even though a general agreement exists regarding the monitoring of some communities (sedimentary and rocky communities; sub-, inter-, and sometimes supratidal communities), motivations and relevance of target species or methodologies do not seem to be much discussed.

In order to identify similarities and differences, *Cedre* is carrying out a synthesis of the oil spill monitoring programmes set up following six major oil spills, namely the "Amoco Cadiz" (1978), "Exxon Valdez" (1989), "Aegean Sea" (1992), "Braer" (1993), "Sea Empress" (1996) and "Erika" (1999) disasters. The objectives of the study are, on one hand, to compare the approaches and methodologies proposed in each case, in order to monitor the impacted communities (plankton and pelagos, subtidal benthos, intertidal communities, supralittoral communities, birds and mammals), and on the other hand, to inventory the targets in terms of habitats, communities, and species. This work aims to identify some common approaches and strategies accepted by the international marine scientist's community.

Keywords: oil spill, ecological impact, monitoring designs.

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The “Prestige” crisis: Operational oceanography applied to oil recovery by the Basque fishing fleet and the study of the long-term environmental impacts

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On 19th November 2002, the oil tanker “Prestige” (containing 77 000 tonnes of heavy fuel n°2 – M100) sank in 3500 m of water, off the coast of northwestern Spain. Intermittent discharge of oil from the stricken tanker, combined with large-scale sea surface dispersion, created a tracking and recovery problem. Initially, conventional oil recovery approaches were adopted, close to the wreck. With time and distance from the source, the oil dispersed dramatically and became less viscous. Consequently, a unique monitoring, prediction and data dissemination system was established, based upon the principles of ‘operational oceanography’; this utilised *in-situ* tracked buoys and numerical (spill trajectory) modelling outputs, in combination with remote sensing (satellite sensors and visual observation). Overall, wind effects on the surface waters were found to be the most important mechanism controlling the smaller oil slick movements. The recovery operation involved up to 180 fishing boats, 9 m to 30 m in length. Such labour-intensive recovery of the oil (21 000 tonnes, representing an unprecedented ratio of 6.6 tonnes at sea, per tonne recovered on land) continued over a 10-month period. The overall recovery at sea by the fishing vessels represented 63% of the total oil recovered at sea; this compares to only 37% recovered by specialised ‘counter-pollution’ vessels. Ongoing research comprises long-term environmental impact studies related to the spill in order to evaluate potential damages and management procedures.

Keywords: Biscay, crisis, fuel, oceanography, oil, operational, “Prestige”, spill.

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ICES CM 2005/S:21 – Poster

Evolution of the PAH content in commercial shellfish from Galicia (NW Spain) after the “Prestige” oil spill

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From January 2003, just two months after the “Prestige” accident (November 2002), commercial shellfish

samples from different areas affected by the spill were collected monthly.

These samples were extracted with a Soxhlet apparatus using a mixture of solvents and cleaned up by column chromatography using deactivated alumina and finally analysed for 13 individual PAHs using HPLC-FLD.

AESA (Spanish Agency for Food Security) has established a guide value for the sum of 6 of these PAHs and no extraction or commercialization of the shellfish could be done over this limit.

The PAH concentrations found were compared with that guide value and this was only exceeded in some sites during the first samplings and reached normal values during the summer 2003.

The sum of 13 PAHs found in these commercial shellfish species were compared with those found in wild mussels from the same samplings and a similar behaviour was observed for all of them.

Keywords: spill, PAHs, hydrocarbons, shellfish.

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ICES CM 2005/S:22 – Poster

Analysis of the Spanish trawl fleet spatial distribution during and post-“Prestige” oil spill by GIS simulations and real data

Esther Abad, J. M. Bellido, A. Punzón, N. Pérez, and M. A. Ámez

Both during and after the “Prestige” oil spill, the Instituto Español de Oceanografía (IEO) carried out a number of research surveys to assess the impact of the oil spill on the living resources; they were named “Prestige” Plataforma 1202, 0103, and 0403. The Spanish Government adopted a series of fisheries management measures, such as fishing closure areas, with absolute banning for fishing, and restrictions for fleet types and gears. The Program of observers on board commercial vessels resumed as soon as management measures allowed it. To determine how and how much these restrictions have affected the use of the traditional fishing grounds and the fishing effort, an analysis of the evolution of the trawl fleet spatial distribution was made. Georeferenced onboard catches and real fleet location, both coming from observers at sea, as well as abundance indices from research surveys, were integrated into a Geographic Information System (GIS). Ancillary data as bathymetry, base-port, and seabed substrate were also included. Simulations on spatial effort distribution were made and checked with real data for comparison and validation. The final aim is to determine the possible effects on changes of spatial effort distribution due to the oil spill.

Keywords: "Prestige" oil spill, fishing effort, spatial distribution, GIS, Cantabrian and Spanish northwestern fisheries.

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ICES CM 2005/S:23 – Poster

Degradation of oil with regard to the Barents Sea

J. H. Pedersen and T. Kristiansen

The currents system of the North Sea is characterized by strong currents and tides, enabling a quick turnover rate of water masses compared to the Barents Sea, where water mass movements are in general slower. Since 1965, over 900 petroleum exploration wells have been drilled in the Norwegian North Sea, while only 70 exploration wells have been drilled in the Barents Sea since 1980. New attention to the Barents Sea as a potential oil and gas province may result in several new exploration wells to be drilled in the near future. Oil spilled on the sea surface will rapidly change composition and properties due to physical and chemical processes, such as spreading, dispersion, evaporation, weathering, emulsification, water washing, and oxidation. Wave action and temperature are key factors. Biological processes include break-down of oil by bacterial oxidation of petroleum. These processes altogether increase the viscosity and gravity of the spilled oil, due to removal of the light components in the oil. Despite the severe alteration of the spilled oil, specific organic molecules are still contained in the oil residue even long time after the spill. These molecules may be used to recognize the source of the oil, and eventually to identify the origin of the oil spill.

Keywords: oil spill, Barents Sea, degradation of oil.

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ICES CM 2005/S:24 – Poster

Microbial detection of hydrocarbon contamination in fish

Stephen O'Neill and Ian M. Davies

Microbial biosensors offer the potential for rapid and relevant analyses of fish samples in the field, providing information which could assist the effective management of oil spill pollution incidents through the identification of contaminated fish. Naphthalenes dominate the PAH profile of crude oils as exemplified by the oil spilt from the MV "Brear" in 1993. Uptake of naphthalenes in fish results in a taint which can be detected in the flesh by sensory assessment. *Pseudomonas fluorescens* HK44 has been constructed to bioluminescence on degrading

specific polycyclic aromatic hydrocarbons (PAH) such as naphthalenes. Research was carried out into the bioluminescent response of *P. fluorescens* HK44 to uncontaminated muscle from a variety of fish species: cod (*Gadus morhua*), saithe (*Pollachius virens*), salmon (*Salmo salar*), rainbow trout (*Oncorhynchus mykiss*), halibut (*Hippoglossus hippoglossus*), and dover sole (*Solea solea*). The bioluminescent signatures suggest that species-specific method blanks are required when using HK44 to detect crude oil and PAH contamination in fish. Two species of marine white fish were spiked with Forties crude oil ranging from approximately 50 to 2560 ng total PAH/ g of halibut muscle and 580 to 93400 ng total PAH/ g of dover sole muscle. A general species-specific pattern of increased luminescence with increased PAH concentration was observed. *P. fluorescens* HK44 response to 580 ng total PAH/ g of dover sole muscle was significantly different from blank fish muscle, while large variation within the halibut data prevented lower spiking concentrations from being differentiated from one another. This research demonstrates the potential of the technique while identifying areas for further improvement. Future work is planned to determine the PAH detection limits in a wider variety of relevant fish species.

Keywords: biosensors, hydrocarbon, PAH.

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ICES CM 2005/S:25 – Poster

May the "Prestige" oil spill have affected mackerel trophic structure?

I. Olaso, B. Villamor, F. Velasco, J. L. Gutiérrez-Zabala, and I. Preciado.

The "Prestige" oil spill introduced hydrocarbons in the water column; their impact on the lower trophic levels of the food web, e.g., the plankton, is not well known. Mackerel is a plankton feeder in spring, and the aim of the present paper is to compare its diet and feeding habits before and after the spill. We compare the composition of the diet and trophic level of mackerel in the springs of 2001, 2002, 2003, and 2004. This information is a first step to explore possible changes in the lower part of the food chain of the Northwest of Spain related with the "Prestige" oil spill.

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ICES CM 2005/S:26 – Poster

Medium-term monitoring of polycyclic aromatic hydrocarbons in mussels of the estuaries of the Basque coast (NE Spain) following the “Prestige” oil spill

Victoriano Valencia, Ángel Borja, Iñigo Muxika, and Andrea del Campo

After the “Prestige” oil tanker wreck, an important fraction of the oil spilled reached the Basque coast in the inner Bay of Biscay. In order to assess the environmental impact of the spill ten series of samples of intertidal mussels (*Mytilus galloprovincialis*) was collected quarterly from winter 2003 till spring 2005 at thirteen locations of the Basque coast. The remainder PAH concentrations in some places are still higher than the concentrations registered before the “Prestige” oil spill. Short-term distribution of the PAH concentrations shows a whole and strong increase in comparison with the average levels recorded in autumn 2002, before the “Prestige” shipwreck. From winter to autumn 2003 the fluctuation of the PAHs concentrations was related to the pulses of the oil arriving at the coast and to the influence of the orientation of the coastline with respect to the main direction of the fuel oil arrival pattern to the Basque coast. The observed medium-term trends are irregular and not unequivocally related to the attenuation of the events of fuel arrival to the Basque coast or with the progression of the fuel removal operations. A similar irregular pattern has been described related to the seasonal variations of diffuse sources of PAH and with the physiology of the mussels. Remobilization of the fuel from several diffuse sources (inaccessible unclean areas) because of winter marine weather as well as mobilization of sediments in some estuaries forced by human works (dredging, restoration) can explain also the fluctuations of the PAH concentrations and some remarkable maxima recorded in winter 2004.

Keywords: “Prestige”, oil spill, hydrocarbon pollution, PAH, *Mytilus*, Basque coast, Bay of Biscay.

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ICES CM 2005/S:27 – Poster

Oil fate during oil spills in the marine environment – mathematical modelling and future needs

Z. Chen, K. Lee, and S. Sultana

Oil spills often occur during offshore and onshore petroleum production and transportation activities. An understanding of weathering properties including the biological processes associated with marine oil spills is essential for effective implementation of cleanup programs. Besides experimental investigation, simulation

involving computing facilities and numerical analysis is often used to examine the fate of the oil and its components in ocean water. This study contains a state-of-the-art review of mathematical models that can be used to predict the magnitude of impacts to the marine environment and provide information required for the selection of spill response options. It indicates that uncertainties and complexities associated with oceanographic, hydrological, meteorological, and biological parameters have restricted mathematical modelling practices. Subsequently, information technologies including remote sensing image processing, geographic information technology (GIS), and global positioning system (GPS) have been proposed to provide a sound support to the simulation of marine oil spills. Using traditional and non-classical methods to quantify different types of system uncertainties is further discussed in this study to show recent advances and future needs of marine oil spill modelling.

Keywords: biodegradation, mathematical modelling, oil spill, uncertainty.

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ICES CM 2005/S:28 – Poster

A fast and simple extraction procedure for polycyclic aromatic hydrocarbons in marine biota: Application to mussel samples from the Cantabrian coast after the “Prestige” oil-spill

J. Sanz-Landaluze, L. Bartolome, O. Zuloaga, and C. Cámara

A new method for the determination of polycyclic aromatic hydrocarbons (PAHs) in complex matrices as marine biota samples is proposed. The method uses an ultrasonic probe sonication as a new tool to assist extraction, coupled to reverse-phase liquid chromatography (RP-LC) with fluorescence detection (FL) for the determination of US EPA 16 priority PAHs. Furthermore, the accuracy and repeatability of the developed method was calculated from certified reference material and compared with results obtained by other determination methods (microwave assisted extraction and GC-MS). This method avoids the main problems encountered in the determination of PAHs in complex matrices such as marine biota, and no clean-up step is necessary. The developed method was applied to the determination of PAHs on biota samples like mussels (*Mytilus edulis*) and oysters (*Crassostrea* sp.) that were sampled in the Cantabrian Sea (Spain). In November 2002, a large oil tanker, the “Prestige”, broke up in heavy seas off Galicia, on the northwest coast of Spain, spilling more than 77 000 tons of crude oil. The oil formed a large slick on the surface of the water that then washed onto the beaches and rocks all along the coast and also affected the sea bed, a process that was accelerated by

tidal movements and ocean currents. The aim was to study the concentration of PAHs on biota samples collected after the "Prestige" oil-spill and compare results with previous data.

Keywords: polycyclic aromatic hydrocarbons, oil spill, extraction techniques, ultrasonic probe, biota samples.

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ICES CM 2005/S:29 – Poster

Bacterioplankton activity off A Coruña (Galicia, NW Spain) after the "Prestige" oil spill in November 2002

Antonio Bode, Nicolás González, Jorge Lorenzo, Joaquin Valencia, Manuel Varela, and Marta M. Varela

The relationships between changes in abundance and activity of natural bacterioplankton communities in relation to fuel concentration in the water column were studied in coastal waters of A Coruña for a one-year period after the "Prestige" oil spill in November 2002. Total hydrocarbons (THC), bacterial abundance, and activity (leucine uptake) were measured at approximately monthly intervals, and the results were compared with those obtained before the spill. Additional information on environmental variability was provided by temperature, chlorophyll-*a*, and total and particulate organic carbon (TOC and POC, respectively). Maximum values of THC (140 ppb) were measured near the coast shortly after the spill, decreasing thereafter. However, sudden increases of hydrocarbons (up to 75 ppb) were detected in summer, particularly near the seafloor. Despite these values, THC contribution to TOC was relatively low and both variables were not correlated. Bacterial abundance and activity were significantly correlated with water temperature, chlorophyll-*a*, and TOC concentrations, but not with THC. The seasonal variation of mean bacterial abundance after the spill was similar to that described before the spill, while bacterial activity appeared significantly enhanced, especially in January–February, April, and July–October 2003. The effect of fuel on bacteria was mostly restricted to the winter months, as subsequent increases of fuel did not always coincide with high bacterial growth rates. The production of plankton blooms near the coast during the end of summer and in autumn appears as the main factor explaining the increase of bacterial growth rates in this period.

Keywords: bacteria, plankton, activity, abundance, biomass, oil spill, NW Iberia.

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ICES CM 2005/S:30 – Poster

Dispersant effectiveness on oil spills – impact of environmental factors

Niranjan Deshpande, Subhashini Chandrasekar, George A. Sorial, and James W. Weaver

When a dispersant is applied to an oil slick, its effectiveness in dispersing the spilled oil depends on various factors such as oil properties, wave mixing energy, temperature of both oil and water, and salinity of the water. Estuaries represent water with varying salinities. In this study three salinity values in the range of 10–34 ppt were investigated, representing potential salinity concentrations found in typical estuaries. Three oils were chosen to represent light refined oil, light crude oil, and medium crude oil. Each oil was tested at three weathering levels to represent maximum, medium, and zero weathering. Two dispersants were chosen for evaluation. A modified trypsinizing flask termed the 'Baffled Flask' was used for conducting the experimental runs. A full factorial experiment was conducted for each oil to investigate the effect of salinity on three environmental factors: temperature (5 levels), oil weathering (3 levels), and mixing energy (150, 200, and 250 rpm). Each experiment was replicated four times in order to evaluate the accuracy of the test. Statistical analyses of the experimental data were performed separately for each of the three oils three times (with or without dispersant). A linear regression model representing the main factors (salinity, temperature, oil weathering, and flask speed) and second order interactions among the factors were accurately fit to the experimental data. Salinity was found to play an important role in determining the significance of temperature and mixing energy on dispersant effectiveness for almost all the oil-dispersant combinations. The impact of salinity at different weathering was only significant for South Louisiana Crude Oil with dispersant 'A'.

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ICES CM 2005/S:31 – Poster

Recruitment of cirripeds after "Prestige" oil spill on rocky shores of Galicia (NW Iberian Peninsula)

Elsa Vázquez, Milagros Penela-Arenaz, Gonzalo Macho, and Esther Pérez-Fernández

One of the most important sublethal effects after an oil-spill on rocky shores is a modification of recruitment pattern and thus a change in community structure. From February 2004 to February 2005 the recruitment of the intertidal cirripeds *Chthamalus montagui*, *Balanus perforatus*, and *Pollicipes pollicipes* was studied at four

locations on rocky shores of Galicia (NW Iberian Peninsula) that were affected at different levels by the “Prestige” oil spill. Our objective was to determine if there were differences in the recruitment patterns of the three species among sites. Recruitment of *C. montagui* and *B. perforatus* was recorded on artificial plates that were collected and replaced with a monthly or fortnightly periodicity. For *P. pollicipes*, seventy adults were collected with the same periodicity to determine recruitment in their peduncle. At all localities the highest recruitment level was reached at the end of the summer for *C. montagui* and during spring and autumn for *B. perforatus*. Nevertheless for both species maximum recruitment in the heaviest oiled locality was significantly lower than at the other sites. The cumulative number of recruits over the year was significantly higher at the control site and significantly lower in the heaviest oiled locality. The recruitment period was also longer-lasting at the control site. The recruitment patterns of *P. pollicipes* at four locations were very similar. Two recruitment periods, one from February to May and another from July to February, could be clearly observed. Nevertheless the cumulative number of recruits over the year was significantly higher at the control site than at the other locations.

Keywords: recruitment, cirripeds, “Prestige” oil spill, Galicia.

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ICES CM 2005/S:32 – Poster

Polycyclic Aromatic Hydrocarbons (PAHs) levels in cultivated and wild mussels from a Galician site (NW Spain) affected by the “Prestige” oil spill

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Adult mussels (*Mytilus galloprovincialis*) were collected in February, June, and November 2003 from indigenous populations from Corme, a location situated in the area most affected by the arrival of “Prestige” fuel oil slicks. Cultivated mussels were also collected in September 2003 at three different depths in order to study if there were differences in the concentrations of PAHs with the depth.

After Soxhlet extraction followed by extracts cleaning using column chromatography with deactivated alumina, PAHs were determined by High-Performance Liquid Chromatography (HPLC) coupled with a wavelength programmable fluorescence detector.

The 13 aromatic compounds studied were: phenantrene, anthracene, fluoranthene, pyrene, benz(a)anthracene, benzo(g,h,i)perylene, chrysene, benzo(e)pyrene, benzo(b)fluoranthene, benzo(k)fluoranthene,

benzo(a)pyrene, dibenz(a,h)anthracene, and indeno(1,2,3-c,d)pyrene.

Wild mussels collected showed a strong increase in the PAH levels in February 2003 in comparison with the levels recorded before the “Prestige” accident. Subsequently the total PAH concentrations decreased in June 2003 but a new increase was observed in November 2003. After the “Prestige” oil spill a change in the individual distribution of aromatic hydrocarbons was observed too.

Cultivated mussels showed an increase of the PAH concentrations with the depth, and the distribution patterns of the 13 analysed PAHs had similar features to the ones shown by the wild mussels after the “Prestige” oil spill.

Keywords: mussels, “Prestige”, HPLC, PAH.

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ICES CM 2005/S:33 – Poster

Levels and evolution of V, Ni and PAHs in mussels after the “Prestige” oil spill

Victoria Besada, Fernando Schultze, José Antonio Soriano, Lucia Viñas, Ángeles Franco, Bruno Cambeiro, and Juan José González

The objective of this study was to estimate the temporal evolution of the concentrations of vanadium and nickel in wild mussels (*Mytilus galloprovincialis*) as well as their relation with the Polycyclic Aromatic Hydrocarbons (PAHs) concentrations in different areas that have been monitored during two years after the “Prestige” accident (13th November 2002).

Analyses were made in pools of mussel soft tissue representing all sizes present in the sampling point. The analysis of trace metals includes a nitric acid digestion in a microwave and V and Ni were analyzed by ETAAS with Zeeman background correction.

After Soxhlet extraction followed by extract cleaning using column chromatography with deactivated alumina, 13 PAHs were determined by HPLC-FLD.

All the analyses have been performed within the quality control system of the laboratory. This includes the use of certified reference materials as well as participation in international intercomparison exercises, such as QUASIMEME, on a regular basis.

When comparing the evolution in the V and the sum of PAH concentrations along the different sampling surveys, a temporal difference of 4–6 months between the occurrences of the maximum of the sum of PAH levels and the maximum of V has been shown. For both

types of contaminants, the concentrations in the mussels decrease quickly, getting to normal values in some months after the accident.

The “Prestige” influence is not clearly shown in the temporal evolution of the Ni concentrations and as expected no variations in the metals concentrations usually analysed in the National Monitoring were observed due to the “Prestige”.

Keywords: “Prestige”, mussel, metals, PAHs.

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ICES CM 2005/S:34 – Poster

Evaluation of the impact of the “Prestige” oil spill using remote sensing and GIS techniques

Luis González, Gema Martínez, Rebeca Lago, and Jesús Torres

The “Prestige” tanker caused a big oil spill off the Galician coast in November 2002. The heavy fuel oil leaked from the vessel and progressively reached the coastal areas during the next months, creating a big environmental and economic catastrophe in the region. This study describes a system for the detection and monitoring of the “Prestige” oil spill on the Galician coast. Remote sensing techniques are applied in order to detect the possible oil slicks, using mainly ENVISAT ASAR radar images. Satellite radar data has proven very useful in large-scale oil spill detection due to its large coverage and the satellite’s ability to image the sea surface independently of light and cloud conditions. The detection results are integrated into a GIS database jointly with other available information proceeding from different sources, including wind data from scatterometer, wind and surface currents data derived from meteorological or oceanographic models, *in situ* data, and visual observations from helicopters, aircrafts, or ships. Data derived in this system are finally fed to a server with the aim of analyzing the spatial distribution and the evolution of the oil slicks in order to assess the ecological impact of the oil spill on the most sensitive coastal areas of Galicia, such as the National Park of the Atlantic Islands. This work has been done in the framework of the CONTINMAR project within the Strategic Action against Marine Pollution of the Spanish Science and Technology Ministry, and it is aimed at designing contingency plans in the event of accidental marine pollution.

Keywords: GIS, remote sensing, oil spill, ASAR.

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ICES CM 2005/S:35 – Poster

The composition and concentration of hydrocarbons in the East Shetland Basin oil exploration and production area

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As part of an assessment of the impact of oil activity in the North Sea, sediments were collected in 2002, from the farfield only, of the East Shetland Basin, utilising a stratified random sampling design. The mean oil (Forties and diesel) equivalent concentrations were all below background ($< 50 \mu\text{g g}^{-1}$ dry weight), with the mean oil equivalent concentrations for Forties ranging from 7.3 to 38.1 $\mu\text{g g}^{-1}$ dw (dry weight) and for diesel ranging from 2.2 to 12.5 $\mu\text{g g}^{-1}$ dw. When normalised to TOC (to remove differences due to sediment characteristics) there were significantly higher concentrations in the eastern zones, indicating that there may have been a greater petrogenic input here. Mean total PAH concentrations were low, ranging from 24.8 to 116.7 $\mu\text{g kg}^{-1}$ dw. The spatial differences observed for the oil equivalent concentrations were not found for the normalised to TOC PAH concentrations. Concentrations are said to be ‘near background’ if the mean concentrations for defined PAHs are statistically significantly below the provisional Background Assessment Concentrations (BACs). This was the case for the East Shetland Basin, indicating that it is ‘near background’ for these individual PAHs. The PAH profiles were dominated by the heavier and more persistent 5- and 6-ring compounds, with high ($> 40\%$) proportions of parent PAHs, indicating a predominantly pyrolytic input. A number of sediments had a UCM (unresolved complex mixture) in their aliphatic hydrocarbon profile, indicative of petrogenic contamination. Selected samples, including all those with UCMs, were analysed for geochemical biomarkers and all, including those with no UCM, showed evidence of petrogenic contamination. The geochemical biomarker profiles indicated that this minor contamination in all zones was from both North Sea and Middle Eastern oils. Comparison with the historic surveys shows that there has been a significant decrease in Forties and diesel oil equivalent concentrations and PAH concentrations.

Keywords: East Shetland Basin, North Sea, PAHs, biomarkers, hydrocarbons, petrogenic, pyrolytic.

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ICES CM 2005/S:36 – Withdrawn

ICES CM 2005/S:37 – Poster

Effects of “Prestige” oil spill upon subtidal soft-bottom macrobenthic communities in the Basque continental shelf

Iñigo Muxika, Víctor Valencia, and Ángel Borja

After the “Prestige” oil tanker wreck, the oil spill reached the Bay of Biscay in a few weeks. The Basque coast, in the southwest corner of the Bay, was also affected by the spill. The main aim of this contribution is to show the effects of the “Prestige” oil spill upon the subtidal soft-bottom macrobenthic communities in the Basque continental shelf. The hypothetical impact was studied by means of the AMBI, the usefulness of which in detecting impacts produced by hydrocarbon pollution has been already demonstrated in some North Sea oil platforms. Results show that total concentration of the 23 PAH congeners determined in the Basque continental shelf sediments is not high enough to produce any acute effect on soft-bottom macrobenthic communities: AMBI values range from 1 to 2.5, corresponding to healthy communities on undisturbed to slightly disturbed sediments. This slight disturbance can be interpreted in terms of natural variability of the area, affected historically by industrial and urban sewage discharges, discarding any deleterious effect produced by the “Prestige” oil spill upon the deep subtidal benthic communities.

Keywords: “Prestige” oil spill, hydrocarbon pollution, AMBI, soft-bottom macrobenthos, Basque coast, Bay of Biscay.

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ICES CM 2005/S:38 – Poster

Sensory assessment of hydrocarbon taint in fish and shellfish from the North Sea

A. D. McIntosh and A. E. Craig

In the event of an oil pollution incident at sea, the response of the relevant authorities must be quick and effective, and also based on sound evidence. Normal response procedures include fish collected at sea to be transported to land-based laboratories for chemical analysis and taint assessment. Petrogenic taint in fish muscle arises mainly from 2- to 3-ring polycyclic aromatic hydrocarbons (PAH). Taint can be detected through sensory assessment, and can render fish unsuitable for the market place.

FRS Marine Laboratory maintains the UK designated, accredited (ISO 17025) facility for sensory assessment of fish and shellfish within the national contingency plan for response to offshore incidents. Petrogenic taint

assessment is performed by a panel of assessors, chosen and trained for their ability to recognise hydrocarbon taint in fish. This report presents baseline data on taint in commercial fish species from the North Sea against which the effects of pollution incidents can be assessed. It also addresses concern that some commercial fish stocks could potentially be tainted by hydrocarbons as a result of routine operation of the offshore oil industry.

Fish and shellfish caught in July/August 2002 in the East Shetland Basin and around the Forties oilfields were assessed for the presence of taint. A total of 70 haddock, 69 lemon sole, and 10 mackerel were sampled from the East Shetland Basin. Forty haddock, 20 lemon sole, and 30 mackerel were sampled on a transect between the East Shetland Basin and the Forties oilfields. Sixty haddock, 50 lemon sole, 25 mackerel, 50 herring, and 160 *Nephrops norvegicus* were sampled in the Forties oilfields. A total of 50 haddock, 80 lemon sole, 20 mackerel, and 10 herring were sampled on a transect between the Forties field and Aberdeen.

No taint was detected in any of the samples assessed.

Keywords: fish, taint, petrogenic, shellfish, oil, sensory assessment.

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ICES CM 2005/S:39 – Poster

Performance of sensory assessment panels for the detection of petrogenic taint in fish

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FRS Marine Laboratory, Aberdeen is the designated facility for sensory assessment of fish and shellfish within the UK national contingency plan for response to offshore incidents, such as hydrocarbon spills. The work is accredited at FRS under ISO 17025.

Assessment of fish and shellfish for petrogenic taint is performed by a panel of assessors, chosen and trained for their ability to recognise hydrocarbon taint in fish. After initial screening, volunteers are specifically trained in the recognition and scoring of hydrocarbon-related taint. Panel members participate in a continuous training programme, in which an assessor-specific reporting system is utilised at bi-monthly intervals to monitor performance. Individual performances are assessed and training records are kept to support and validate the panel members' continuing expertise. The training utilises parallel samples of fish tissue, which are analysed chemically for polycyclic aromatic hydrocarbon (PAH), and also assessed by the panel.

In order to develop our statistical understanding of the sources of variance in the panel scores, three sets of statistical mixed models have been applied to the training

session data, and used to calculate various factors including between-session and between-assessor variances. A good panel should optimally have low between-session and between-assessor variation. Current indications are that the main sources of variance are between-assessor factors, i.e., individual assessors are relatively consistent in their scoring patterns, but significant differences exist between assessors.

Possible training strategies to reduce the between-assessor variance include the use of reference samples of known level of taint during panel sessions, emphasising the availability of the full range of taint scores, or the adjustment of individual scores using pre-determined assessor-specific relationships between score and PAH contamination.

Keywords: sensory assessment, petrogenic taint, fish.

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Distribution of hydrocarbons in the Fladen Ground

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This paper presents the results of investigations carried out into the effects of oil exploration and production in the Fladen Ground, northern North Sea on the distribution and composition of hydrocarbons in sea bed sediment. A stratified random sampling design was used, covering 16 Zones of equal size. The mean oil (Forties or diesel) equivalent concentrations were all below 'background' ($< 50 \mu\text{g g}^{-1}$ dry weight) ranging from $7.4 \mu\text{g g}^{-1}$ dry weight (SE = 0.4) in Zone 13 to $22.2 \mu\text{g g}^{-1}$ dry weight (SE = 1.3) in Zone 11 for the Forties crude oil equivalents, and $2.2 \mu\text{g g}^{-1}$ dry weight (SE = 0.1) in Zone 13 to $7.0 \mu\text{g g}^{-1}$ dry weight (SE = 0.6 and 0.8) in Zones 4 and 5 for diesel oil equivalents. The mean total PAH concentrations (2- to 6-ring parent and alkylated PAHs including the 16 US EPA PAHs) in sediments ranged from $53.9 \mu\text{g kg}^{-1}$ dry weight (SE = 2.8) in Zone 13 to $206.6 \mu\text{g kg}^{-1}$ dry weight (SE = 23.0) in Zone 4, the PAH concentrations were generally higher in the Zones of higher percentage $< 63 \mu\text{m}$ particle sizes fractions and organic carbon content. The PAH distribution profiles and concentration ratios in the Fladen Ground indicated a predominantly pyrolytic input, being dominated by the heavier, more persistent 5- and 6-ring compounds, and with a high proportion of the parent PAHs. The mean total *n*-alkane ($n\text{C}_{12}$ - $n\text{C}_{33}$) concentrations ranged from $55.4 \mu\text{g kg}^{-1}$ dry weight (SE = 7.6) in Zone 13 to $206.8 \mu\text{g kg}^{-1}$ dry weight (SE = 49.5) in Zone 8. The *n*-alkane profiles of a number of the sediments showed a small, high boiling point UCMs, indicative of limited petrogenic input from weathered oil. The geochemical biomarker profiles of the sediments (containing UCMs) contained a small bisnorhopane peak and a high

proportion of norhopane to hopane, indicating that there was contamination from both Middle Eastern and North Sea oils, and therefore not solely as a result of oil exploration and production activity in the area. The most likely source of petrogenic contamination was from shipping.

Keywords: North Sea, Fladen Ground, PAHs, sediment, oilfields, *n*-alkanes, Forties.

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Tidal flat macrobenthos resistance to medium-term emersion: the case of the "Tricolor" oil pollution prevention in the Zwin nature reserve (Belgium)

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As a result of the impending "Tricolor" oil pollution in the Southern Bight of the North Sea at the end of January 2003, the Zwin nature reserve was blocked from the North Sea by use of a sandbarrier. This method of protection has an important consequence for tidal flat ecosystems: the absence of the tide. Because the effects on the important bottom-life of the tidal flats could not be estimated beforehand, the damming up was taken as the ideal opportunity to study these effects. To estimate the effects of the tideless situation, macrobenthic samples were collected starting just before, two times during (after 12 and 21 days of emersion), and frequently, after the removal of the sandbarrier, during one year. This study shows a high resistance of all macrobenthic species to a medium-term emersion during winter. Two ecological patterns could be distinguished during the emersion: (1) immigration into the emersed intertidal zone of *Talitrus saltator* and *Orchestia gammarellus*, (2) decreasing densities of polychaete species which were very abundant before the construction of the sandbarrier. However, both patterns were not significant. Therefore, in view of the high survival of the macrobenthos to a medium-term emersion and the fact that oil pollution in the nature reserve was inhibited, damming as a measure against oil pollution in winter may be positively evaluated.

Keywords: tidal flat macrobenthos, "Tricolor" oil pollution, Zwin nature reserve, emersion, mortality, immigration.

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Concentrations of polycyclic aromatic hydrocarbons (PAHs) in sediments on the Spanish coast, one year after the “Prestige” fuel-spill

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A study on the levels and the evolution of the pollution derived from the “Prestige” oil spill that took place in front of the Galician coast on November 2002 is being carried out. In this work the results of the PAH concentrations in the surficial sediment in 2004, from the entire Spanish coast, following the “Prestige” oil spill are presented.

The sampling was carried out using the RV “Cornide de Saavedra” during the months of February and September 2004. The station depths varied between 30 and 250 m, whereas the distance from the coastline was in the range of between 3 and 20 miles.

The compounds analysed were: phenanthrene, anthracene, fluoranthene, pyrene, benz[*a*]anthracene, chrysene, benzo[*e*]pyrene, benzo[*b*]fluoranthene, benzo[*k*]fluoranthene, benzo[*a*]pyrene,

dibenz[*a,h*]anthracene, benz[*g,h,i*]perylene, and indeno[*1,2,3-c,d*]pyrene.

The 13 analysed PAHs were separated by means of High Performance Liquid Chromatography (HPLC) with a gradient of methanol-water as mobile phase. The identification and quantification was carried out using a fluorescence detector with programmable wavelength, multilevel calibration, and 2-methyl-chrysene as internal standard.

Analyses were conducted within a strict internal and external analytical quality control scheme for both sediment and biota. Results obtained in both ways guarantee the quality of the data obtained by this laboratory.

Some areas in the Gulf of Biscay have suffered some important industrial facilities, since the beginning of the 20th century. This can explain the PAH levels in sediments, one or two orders of magnitude higher than in Galicia. For that reason, the “Prestige” spill effect is clearer on the Galician coast.

Keywords: PAHs, spill, sediment.

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