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PETROLEUM HYDROCARBONS IN COCKBURN SOUND

A report to
BP Refinery (Kwinana) Proprietary Limited
and the
Department of Conservation and Environment
Western Australian

by the
Petroleum Geochemistry Group, WAIT
edited by
Robert Ian Kagi
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Department of Conservation and Environment
Perth, Western Australia

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THE WESTERN AUSTRALIAN DEPARTMENT OF CONSERVATION AND ENVIRONMENT

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THE PETROLEUM GEOCHEMISTRY GROUP, WAIT
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PREFACE AND ACKNOWLEDGEMENTS

A large number of people collaborated in the conduct of this study. Management of the program was the responsibility of a steering committee consisting of representatives of BPRK (Roger Macrae, David Lea, and Mark Wheeler), of DCE (Graham Chittleborough and Victor Talbot) and of WAIT (Bob Kagi, Bob Alexander and Max Offer). Bob Kagi prepared each of four progress reports and this final report.

Ron Hogg began work on the program in 1980, and when he left, Max Offer proceeded to carry out the bulk of the chemical analysis during 1981 with assistance from Mark Cumbers and Ray Taylor. Other staff of the Petroleum Geochemistry Group and the School of Applied Chemistry at WAIT also provided assistance from time to time. Supervision of these aspects of the program was shared by Bob Alexander and Bob Kagi. Frank Flannigan and Glenda Raymond of the Department of Home and Consumer Studies, WAIT carried out the organoleptic studies. Assistance from DCE (Victor Talbot, Mike Ford), BPRK (Mark Wheeler) and WAIT (Brian McGuire) with collection of samples is gratefully acknowledged.

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AIMS OF THE STUDY

1. To measure the present levels and principal constituents of petroleum derived hydrocarbons being discharged by the BPRK refinery at its four outfalls.

2. To establish the pattern and extent of the mixing zone in the receiving waters of Cockburn Sound.

3. To measure the quantities and constituents of the petroleum-sourced material in selected species of the marine biota and to compare these levels with those immediately outside the Sound and elsewhere, in order to put these results into perspective.

4. To check by controlled testing whether tainting occurs in fish and to correlate the results with chemical analysis of the fish.

PROJECT EXECUTION

The project was carried out at WAIT in the period March, 1980 to November, 1981. Chemical work was carried out in the School of Applied Chemistry and organoleptic studies were carried out in the School of Home and Consumer Studies. Coordination of the project was the responsibility of a steering panel consisting of representatives of BPRK, DCE and WAIT. Funding was provided by BPRK ($15 000) and DCE ($10 000).

OUTCOME OF THE PROJECT

Hydrocarbons in BP Refinery Effluent Waters

Effluent waters were sampled on seven occasions. Levels of hydrocarbons were determined by solvent extraction and concentration of the extract, followed by analysis using UV fluorescence or capillary gas chromatography. A sample of oil collected from Tank 4, the unit in which all oil skimmings from the refinery effluent treatment units are accumulated, was used as a standard. The values obtained were highly variable and tended to be similar but slightly lower than those obtained by BPRK using IR analysis of a carbon tetrachloride extract. The differences between procedures is not surprising considering that there are substantial differences between the analytical protocols. Based upon the information presently to hand, the burden of petroleum to the Sound typically falls within the range 26-2600 kg/day. BPRK staff estimate that loadings average approximately 500 kg/day. This variability from time to time of the petroleum burden of the effluents reflects changes in refinery operation and highlights the difficulty in determining a notion of the burden of petroleum entering the Sound. This difficulty is compounded by two other factors. The first is that superimposed on the chronic burden from API-1 and South Outfall which is itself variable, there are intermittent and often unpredictable pulses of petroleum entering the Sound from Circular Seperators via Centre Outfall and South Outfall. The second factor is that there remains considerable uncertainty about the volume of water flows from Central Outfall and South Outfall.

Hydrocarbons in the Sound Receiving Waters

On three occasions, under different regimes of wind conditions, water samples were collected in and around the effluent plume at a depth of 50 cm. Petroleum levels were determined by comparison with samples of oil collected from Tank 4 on the same day using UV fluorescence and capillary gas chromatography. Apart from one occasion on the 16th October, the agreement between UV fluorescence and gas chromatography values was surprisingly good. The discrepancy on 16th October is attributed to the emission of a pulse of material with different UV properties. There is clearly a fairly rapid diminution of petroleum levels. Outside a zone 1-2 km from the outfall, the levels are unlikely to greatly exceed those found elsewhere in the Sound (approximately 1 ug/l). A number of processes are likely to contribute to the diminished concentration. The gas chromatograms suggest strongly that volatile material is lost to the atmosphere by evaporation, and higher molecular weight material is likely to be adsorbed onto particulate matter and is eventually incorporated into the sediments.

Hydrocarbons in Mullet

Composite samples of a number of individual mullet caught in the effluent stream within approximately 50 m from the shore at BPRK outfall, and adjudged by the tasting panel to be highly tainted, were extracted and hydrocarbon fractions were isolated. These mullet showed greatly enhanced levels of petrogenic material compared with those found in untainted fish from Warnbro Sound. Comparative values were 15 mg/kg and less than 4 ug/kg of aromatics, and 15 mg/kg and 0.2 mg/kg of saturates. The tainting of the Cockburn Sound mullet was therefore attributed to the enhanced levels of petroleum hydrocarbons, particularly aromatics. Closer inspection of the gas chromatograms reveals a number of interesting aspects which might have some management implications. Firstly, there are increased levels of biogenic alkanes in Cockburn Sound mullet, a fact which may be attributed to increased microbiological production of these materials in the Sound due to the greatly increased nutrient status of the Sound. Secondly, and more importantly, aromatics in the mullet are almost exclusively the more soluble, lower molecular weight benzene and naphthalene derivatives. These compounds are among the more toxic components of petroleum. The fact that they are also very volatile suggests possible simple and cheap effluent treatment options to reduce the hydrocarbon burden to the Sound , lower the toxicity of the contained hydrocarbons, and reduce the tainting of fish in the vicinity of the BPRK Outfall. Consideration of these is however, beyond the terms of reference of the present study.

Hydrocarbons in Mussels

Alkanes and aromatic hydrocarbons were isolated from samples of mussels from Beacon Head and from a bottom site approximately 250 m southwest of the BPRK outfall in water approximately 2.5 m deep. In the mussels from near the outfall, the levels of alkanes were enhanced by approximately one order of magnitude, and the levels of aromatics by at least three orders of magnitude, over those found in the Beacon Head mussels. In both cases, the chromatograms are very complex, and show the presence of higher molecular weight petrogenic material. This might be attributed to mussels which are filter feeders ingesting the more persistent, less soluble, less volatile, higher molecular weight material in the effluent which, rather than evaporating, is adsorbed onto particulate material in the water. The levels of a number of specific polynuclear aromatic compounds and groups of these compounds were determined by gas chromatography-mass spectrometry in the sample of mussels from near the BPRK outfall. They were not detectable in the sample of mussels from Beacon Head using this technique. The values of approximately 50 mg/kg (wet weight) petroleum hydrocarbons, and 5 mg/kg polynuclear aromatics found in the mussels 250 m from the BPRK Outfall are consistent with levels recorded in the literature for areas subject to contamination with petroleum. The value of 7 ug/kg for the carcinogen benz(α)pyrene again is similar to those found in studies of contaminated areas, but is up to several orders of magnitude lower than those reported in severely polluted sites.

Tainting of Fish in Cockburn Sound

Collection of fish for organoleptic and chemical evaluation was carried out on three occasions. Difficulties were experienced in obtaining adequate quantities of matched samples of fish from control sites and sites adjacent to the BPRK outfall, however a number of conclusions have been reached. Fish captured in the warm waters of the effluent plume within approximately 50 m of the BPRK outfall were likely to be tainted, some to a profound degree. On the other hand, fish captured 1 km or further from the outfall were not adjudged tainted by tasting panels.

CONCLUSIONS

The project has provided answers to each of the specific aims set down as objectives at the commencement of the study. BPRK are presently carrying out significant alterations to their processes and treatment facilities. These are expected to further reduce effluent petroleum levels and also to permit closer monitoring of the effluent treatment facilities. It is probably not appropriate that any further studies be carried out until these innovations are completed.

1. INTRODUCTION

1.1 Background to the Present Study

Cockburn Sound is located on the west coast of south-western Australia, immediately to the south of the capital, Perth, a city of just under one million people. A location map of the study area is shown in Figure 1. Generations of Western Australians have enjoyed the Sound for recreational activities such as swimming, fishing, sailing, and family outings, and it supports a small professional fishery. From the middle 1950's heavy industry has been building up on the eastern shores of the Sound, taking advantage of the naturally protected waters for port facilities. Significant developments from the point of view of the present study include the BPRK oil refinery (1955), the sewerage primary treatment plant at Woodmans Point (1966), the CSBP superphosphate plant (1968), and the KNC plant manufacturing ammonia, nitric acid and ammonium nitrate (1968).

The first major signs of deterioration of the Sound appeared in the late 1960's with the commencement of the decline of the Posidonia seagrass meadows, so that by the mid 1970's approximately 80% of the original area had died: periodic algal blooms began to appear in the early 1970's. In 1976-1979 a three-year environmental study[1] was carried out to provide a basis for future management of the Sound. This study demonstrated that Cockburn Sound behaves much like a tidal lake, and as a result steps are in hand to greatly reduce emissions into the Sound waters, particularly of nutrients, heavy metals, and bacteria from sewerage. The present study of petroleum contamination in Cockburn Sound developed out of a preliminary survey carried out in the context of the major study in 1979[2].

1.2 Aims of the Study

The aims of the study were:

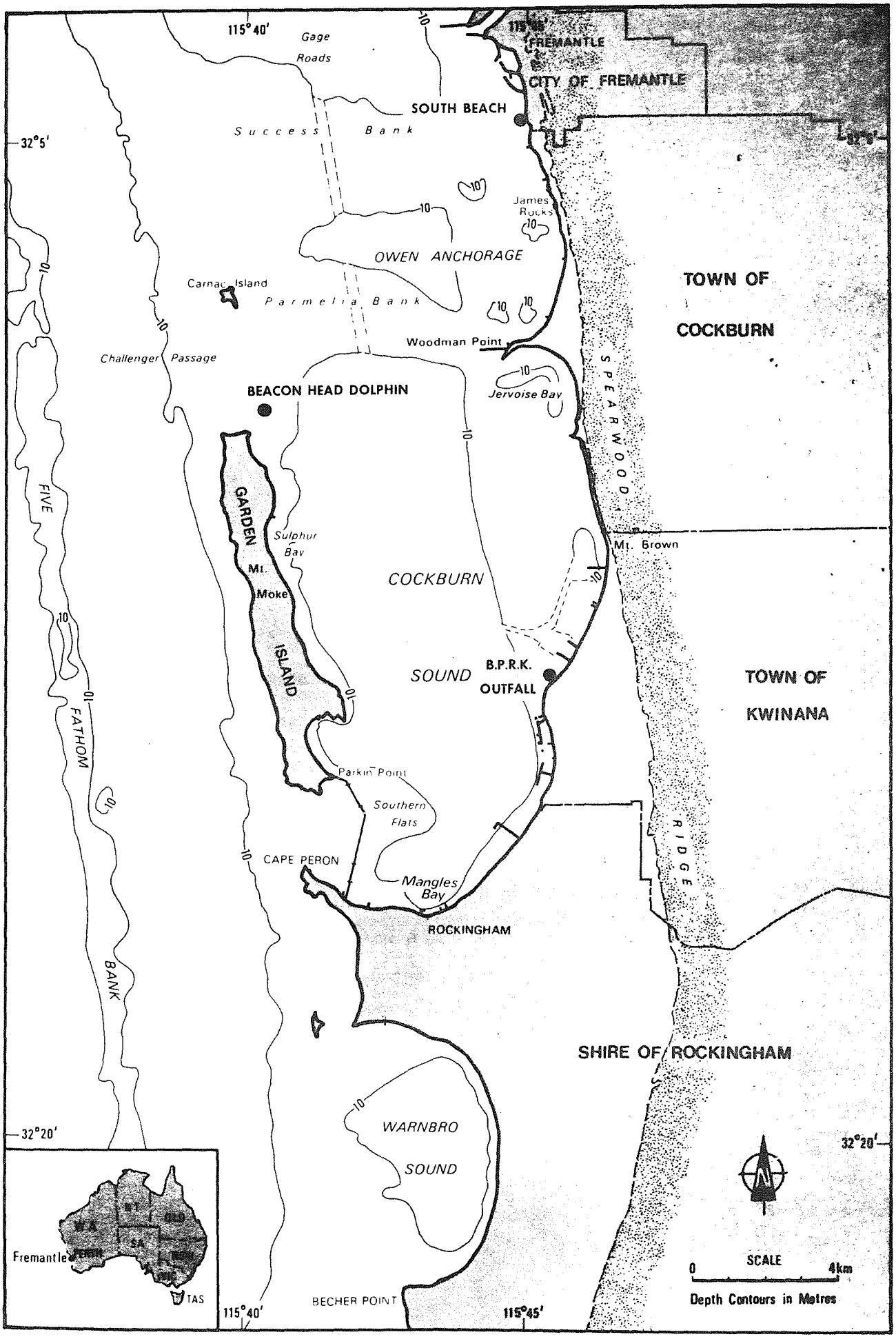
1. To measure the present levels and principal constituents of the petroleum-derived hydrocarbons being discharged by the BPRK refinery at its four outfalls.

2. To establish the pattern and extent of the mixing zone in the receiving waters of the Sound.

3. To measure the quantities and constituents of the petroleum-sourced material in selected species of the marine biota, and to compare these levels with those immediately outside the Sound and elsewhere in order to put these results into perspective.

4. To check by controlled testing whether tainting occurs in fish, and to correlate the results with chemical analysis of the fish.

Figure 1: Cockburn Sound and adjacent areas



1.3 Project Execution

The project was carried out at WAIT in the period March 1980 to November, 1981. Chemical work was carried out in the School of Applied Chemistry and organoleptic studies were carried out in the School of Home and Consumer Studies. Coordination of the project was the responsibility of a steering panel consisting of representatives of BPRK, DCE and WAIT, which considered four progress reports. Funding was provided by BPRK ($15,000) and DCE $10,000).

1.4 The BP Refinery at Kwinana

The BP refinery at Kwinana was first opened in 1955. It is the only oil refinery in Western Australia, and its capacity of approximately 5.3 million tonnes per year of crude oil and 120,000 tonnes per year of lube oil makes it among the largest in the country. The refinery processes a variety of up to about twenty crudes, principal among which are Iranian, Barrow Island, Kuwait, Murban and Handil. The organisation of water flows in the refinery is outlined in Figure 2. Significant features are that excepting for tanker ballast water which flows into Circular Separators, all refinery process waters and similar oily waters flow via a sewer system into API-1, a gravity separator, where the bulk of the oil is separated. The effluent water then passes to Sewer Box 33 where it is mixed with a large volume of cleaner water from the Circular Separators and the resulting diluted stream emerges at South Outfall. Prior to entering the Sound, this water is vigorously mixed with cooling water, principally from BP No. 1 (catalytic cracker). Caustic washes containing mercaptans and phenolics are collected in Tank 3 and are released continuously into the forebay of the Circular Separators, and thence into the Sound via the Centre and South Outfalls. All oil skimmings from separation units are collected in Tank 4, so this may therefore be expected to reflect the composition of the oil in recent effluent. The performance of API-1 has been improved since the initial Cockburn Sound Study with the installation of an oil retention baffle in the forebay and other modifications. There are substantial uncertainties in the values for certain flows shown in Figure 2. In particular, the values of 6 megalitres per day and 80 megalitres per day flows into Sewer Box 33 from API-1 and South Circular are only very crude approximations. The flows from API-1 especially might be expected to vary widely with changes in refinery operations and weather conditions. This situation effectively confounds attempts to determine either the total petroleum burden or the contributions to the petroleum burden of the effluent made by each of the four treatment units in anything other than the crudest manner. Installation of a testing station comprising a V-notch weir to measure water flows and a sump to induce turbulence to enable collection of a homogeneous sample for analysis at the exit point of API-1 is presently in hand. These developments will enable the performance of the unit to be measured directly.

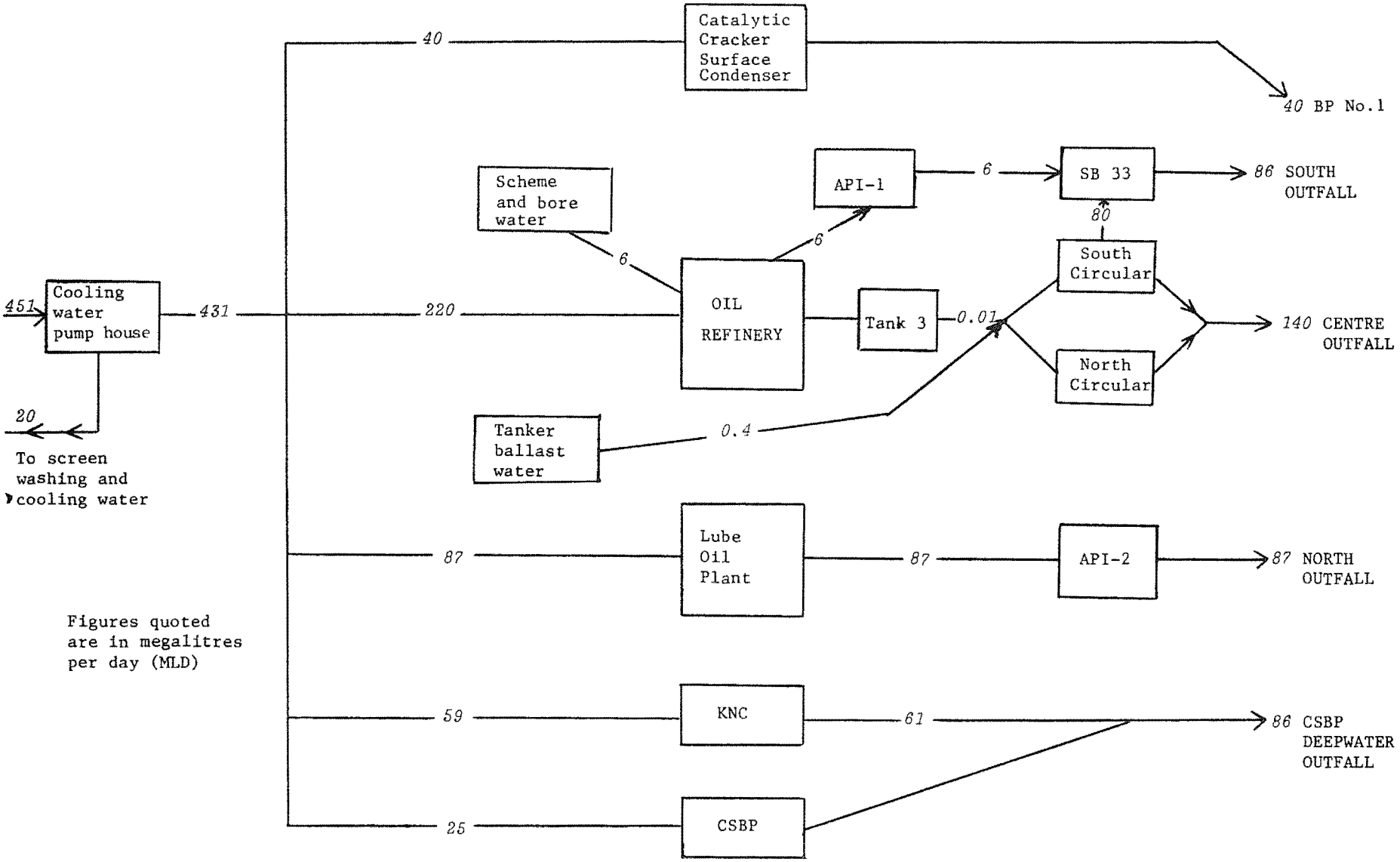


Figure 2: Approximate water flows in BPRK Refinery

The management of BPRK has a policy of gradual improvement of the performance of API-1. Minimising the flows of oil and water into the system and limiting the use of surfactants which cause the formation of emulsions are two improvements which have been made. Further, a number of process operations are in hand which will greatly reduce the quantities of spent caustic waste with its contained phenols and mercaptans which passes into the Sound in the effluents.

1.5 Petroleum in Natural Water Bodies

Petroleum is a complex mixture of different compound types which at low levels vary greatly in their impact on the environment[3]. Alkanes have a low toxicity, many occur widely in natural systems, and they are biodegraded comparatively rapidly[3]. Aromatics such as the naphthalenes on the other hand have a much higher toxicity to biota both on acute and chronic exposure, and are much less rapidly biodegraded[3]. Together with the rather ill-defined oxygen-, nitrogen-, and sulphur - containing compounds which are usually present in oil in small quantities, aromatics are the more organoleptically potent components of petroleum. Polynuclear aromatic hydrocarbons and their sulphur and nitrogen analogues (PNA's) are also present in petroleum and petroleum products. These compounds are very resistant to biodegradation; because they have limited solubilities in water they tend to be adsorbed on particulates in water, and they are therefore accumulated in filter feeders such as mussels and oysters[3,4]. Many PNA's have been shown to be potent carcinogens.

Much of the work reported on analysis of water contaminated with petroleum has involved studies of point sources arising from foundering tankers, oil well blowouts, or similar episodes[4,5,6]. In these situations, it may be possible, although technically challenging, to fully characterise the petroleum source, to observe its behaviour in the water column under the effects of weathering, and to monitor its levels in biota. A refinery effluent stream is a quite different source of petroleum contamination in that a variable oil burden of continuously variable composition, well-mixed with a stream of warm effluent waters, is released into the receiving waters. The fate and effects of oil contained in such an effluent stream is likely to be quite different from that of bulk oil released into receiving waters as in a typical spillage incident. In such circumstances it is possible to regulate levels of oil release by legislation, however, with the limited knowledge of subtle effects of chronic exposure to low levels of petroleum, the setting of permitted discharge levels is a difficult matter.

A further challenge in assessing a situation involving petroleum contamination of a water body is that the processes of weathering modify the nature of the contaminant at a rate which varies greatly with water temperature, wind, sea state, and other environmental factors[7,8,9,10]. The physical changes which occur are: spreading or extension over the water surface; movement or drifting; evaporation of more volatile constituents; dissolution and dilution of more water-soluble components; emulsification and dispersion; adsorption onto particles; absorption into organisms; and sedimentation[8,10]. Evaporation and solution are competing processes which leave a similar residue - the higher molecular weight, less volatile, less-soluble components of the oil. The effects of these two processes upon the marine ecosystem are however quite different, as the more soluble low molecular weight material, particularly the aromatics, is more acutely toxic than other hydrocarbons[3], and when dissolved it is available for uptake by marine organisms. A number of studies[8,10] have indicated that loss of volatile material from a surface film is a rapid process - half-lives of minutes to hours are indicated for compounds in the range C_6-C_{10}, rising to hours and days for material in the range C_{15}-C_{20}. In the weathering of a surface film, indications are that evaporation might occur two to four orders of magnitude faster than dissolution. The vigorous mixing of a petroleum-contaminated effluent with large volumes of water, whilst reducing the formation of an oil slick, may have the effect of greatly increasing levels of finely dispersed and dissolved petroleum, and as a consequence any toxic effects of the effluent may be enhanced. On the other hand, vigorous mixing probably also promotes evaporation at the mixing point and certainly would increase oxygen levels, thereby possibly enhancing the potential for biological degradation.

Chemical degradation processes which typically involve oxygen and often are photo-induced are known to occur to modify petroleum giving rise to alcohols and acids which are more rapidly biograded and removed more rapidly from the water column[3]. Broadly speaking, biota may effect changes to petroleum in two ways. The first process is physical absorption, leading either to incorporation into the body tissues or excretion perhaps in a modified form with altered properties, for example faecal pellets which may pass into the sediments where further changes may occur[7]. The second process is biodegradation wherein microorganisms, principally bacteria, yeasts, and filamentous fungi ingest and metabolise the hydrocarbons[9,10]. More-soluble hydrocarbons are biodegraded more rapidly than less-soluble hydrocarbons of the same type, and the order of decreasing rate of biodegradation is normal alkanes, branched alkanes, cycloalkanes and aromatics[8,10]. Certain polycyclic compounds are more resistant to biodegradation. These include the polynuclear aromatics[11,12], methyl-substituted dibenzthiophenes[4], triterpanes[13,14], and sterane-type hydrocarbons[13]. Conditions which favour high rates of biodegradation are warm oxygenated water, high levels of nitrogen and phosphorous nutrients, and continued exposure to petroleum in order that integrated colonies of petroleum-degrading microorganisms are developed[9]. One might therefore expect that biodegradation could play a major role in controlling the buildup of levels of hydrocarbons in Cockburn Sound when nutrient levels are very high.

1.6 Analysis of Petroleum Hydrocarbons in Natural Waters

Rigorous assessment of petroleum contamination of a water body requires unequivocal identification of petrogenic material, and measurement of the levels of this material in the system under examination. In some circumstances this task can be complicated when there is a possibility of hydrocarbon contamination from natural marine seepage or from terrestrial anthropogenic sources; however, marine seepages are a most unlikely possibility in the case of Cockburn Sound. The major complicating factor in the Cockburn Sound situation, apart from the variation in the composition of the BPRK effluent, is the presence of biogenic organics in the water, biota, and sediments: the high levels of nutrients in the warm Sound waters has produced high levels of microorganisms which will not be reduced until the planned reduction of nitrogen input, principally from KNC and the sewerage treatment works, is implemented[1].

Seawater and marine organisms contain a wide range of biogenic hydrocarbons[15,16,17], and there are substantial differences between species: values of biogenic hydrocarbons reported range from 20ppm to 4800 ppm dry weight. Alkenes are major hydrocarbon components in algae, and polyenes with either straight chains, branched chains, or isoprenoid structures are also prominent. Straight chain alkanes, especially the odd carbon-number series n-C_{15}, n-C_{17}, n-C_{19}, n-C_{21}, are present in marine phytoplankton. Equal amounts of odd carbon-number and even carbon-number alkanes between C_{25} and C_{32} have been reported in bacteria. Branched alkanes are also found in marine organisms: pristane is the most abundant alkane in some fish; however phytane, its C_{20} analogue, is not commonly found in most biota.

A number of approaches are available for demonstrating contamination of a location with petroleum. One is to carry out analytical measurements, such as ultraviolet fluorescence spectroscopy (UVF), infrared spectroscopy (IR) or gas chromatography (GC) on samples from the subject location. The values obtained can then be compared with those obtained from samples from a pristine, uncontaminated area, and the differences may then be conditionally attributed to pollution. Whilst measurements of these gross parameters may give strong indications of levels of contamination, they suffer from the major difficulty that the analyst does not really know what species are being measured. There are other deficiencies in this approach. For example, in the UV fluorescence technique, unidentified fluorescent components of the oil which may perform in the water column quite differently from other components in the oil, are used as a surrogate for the whole oil. Again, the IR and GC techniques are subject to interference from biogenic material, and also random contamination of samples may not be readily identified. If allowance is made for these deficiencies, these techniques can be very useful, particularly the highly sensitive and rapid UV fluorescence procedure, especially when it is applied in a total fluorescence mode[18]. Gas partitioning[19,20] and

HPLC-UVF[21] are particularly useful for investigating more volatile components of petroleum and polynuclear aromatics respectively. The development of high resolution capillary gas chromatography columns of 10^5 theoretical plates, and gas chromatograph-mass spectrometer units coupled to a computer with a data system (GC-MS-DS), both afforded quantum jumps in analytical power. When used together they represent the most powerful forensic tool available to the petroleum analyst.

A major task in a study of petroleum contamination is the analysis of petrogenic material in the presence of biogenic material. In the maturation processes of diagenesis and catagenesis, organic material undergoes changes to give compounds which are not found in recent biogenic material, and hence can be used to distinguish petrogenic hydrocarbons in the samples. Gross differences which occur may be summarised as follows:

- Odd-even preference (OEP) of n-alkanes[21]. In mature crude oils, the OEP is close to unity in the range C_{10}-C_{20}. Recent biogenic material typically contains predominantly odd numbered n-alkanes, especially C_{15}, C_{17}, C_{19} and C_{21}.

- The unresolved complex mixture (UCM)[21]. Mature petroleum usually contains a vast number of isomeric and homologous branched and cyclic alkanes. This gives rise to a broad envelope in the gas chromatogram which is particularly evident in weathered samples and contrasts with the alkane fraction of biogenic material which typically comprises a series of individual peaks with baseline resolution.

- Pristane-phytane ratios[16]. Whereas biogenic samples typically contain substantial amounts of pristane, phytane, the C_{20} homologue is noticeably less abundant.

- Aromatics[4,11,12,22]. Aromatic compounds such as methyl-substituted naphthalenes, phenanthrenes, and dibenzthiophenes are prominent components of crude oils and are not typically present in hydrocarbons produced by biota. Polynuclear aromatics are very resistant to biodegradation and this group therefore is a very useful class of marker compounds for petroleum contamination.

During maturation, more subtle changes also occur which lead to structural rearrangements and changes in configuration at chiral centres in a variety of classes of compounds[23]. Biogenic acyclic isoprenoid alkanes retain the stereochemistry of the phytol from which they are derived. Material which has undergone maturation shows a loss of this stereospecificity, and the diastereomers can be resolved into a number of peaks using high resolution capillary gas chromatography. For example, pristane and phytane both appear as a doublet, the front peak of which is due to fossil isomers. As has been pointed out by Gassman[24], this method has two considerable advantages: it is very sensitive in that it focusses on compounds which are abundant both in

biogenic material and in petroleum, and it does not require the use of an expensive GC-MS-DS system. Molecular geochemical studies of steranes, diasteranes, and triterpenes applied to environmental problems is presently finding wide use, particularly in fingerprinting petroleum residues so they can be attributed to a particular source[13,14,25,26].

1.7 Effects on Marine Organisms of Chronic Exposure to Low Levels of Petroleum

The effects on marine organisms of exposure to sublethal levels of petroleum has been the subject of a number of recent reviews[3,10,12,27]. Uptake of petroleum may occur by passage across the gills, or by ingestion of contaminated particulates such as food organisms or sediments. The hydrocarbons once ingested may be accumulated, excreted unchanged or metabolised to more polar species which may then be excreted. Effects noted on biota include behavioural changes and physiological effects. Typically, bacteria, algae, and invertebrate animals are more susceptible than vertebrates, behavioural effects being noted at exposure levels in the low ug/l range in the former and mg/l range in the latter group. Physiological effects are typically noted in fish at concentrations in the low mg/l range; however eggs, embryos, and larvae have been shown to be affected by hydrocarbon levels one to two orders of magnitude lower.

In broad terms then, one might expect marine organisms to show adverse effects to chronic exposure to petroleum at concentrations in the range 10-1000 ug/l. The present state of knowledge in this complex field is still a long way from providing simple answers to the question. How much is too much?

1.8 Tainting of Fish by Petroleum

In view of the potential social and economic impact, there are suprisingly few records of studies of tainting of fish by petroleum and related substances. In 1973, Ogata and Miyake[28] documented odour problems in fish from Mizushima Bay, near Okayama in Japan. They attributed these odours to low molecular weight aromatics in effluents from petroleum and petrochemical industries which were discharged into the bay. More recently, Connell[29,30] investigated a kerosene-like taint found in mullet in the Brisbane River and adjacent coastal areas. On the basis of gas chromatography of whole steam-volatile fractions from tainted fish, sediments, and commercial kerosene, the taint was attributed to a kerosene-like material in the sewerage effluent from the city of Brisbane.

2. MATERIALS AND METHODS

2.1 Analytical Methods

General. Prior to use, clean glassware was washed with distilled water, dried, and rinsed with purified dichloromethane. Solvents were prepared by distillation of commercial analytical reagent material, followed by analysis for contamination by capillary gas chromatography. Fluka 100-mesh silicic acid was washed with ether, then pentane, dried at 100°C, then activated by heating at 200°C. The column was eluted with pentane prior to use. Blanks were routinely carried out on all procedures.

Ultraviolet Fluorescence (UVF). Ultraviolet fluorescence determinations were carried out using an Hitachi 650-10M fluorescence spectrophotometer with an excitation wavelength of 310 nm and emissions were measured at 374 nm. Under these conditions, the standard Tank 4 oil showed a linear response in the range of 0-100 ug/ml. The response ratio of chrysene to each standard sample from Tank 4 was determined. Values obtained during the study ranged between 3.5 and 10. In one trial experiment, Tank 4 oil was added to seawater and extracted as described in the procedure. The fluorescence measurements on the extract were within 10% of those of the standard oil. With water samples of 3.3 l, the limit of detection of the method was approximately 1 ug or a concentration of 0.3 ug/l in the water sample.

Liquid Chromatography (HPLC). Liquid chromatography was carried out using a Varian 8500 dual pump LC system equipped with a Variscan variable wavelength UV detector set at a wavelength of 276 nm. Preparative chromatography to prepare samples for further analysis was carried out using a Merck Lobar Grobe A (240-10) Lichroprep Si 60 40-63 um column. The solvent used was hexane-dichloromethane (7:1) at 2 ml/min.

Capillary Gas Chromatography (GC). Capillary gas chromatography was carried out using a Varian Series 1400 gas chromatograph equipped with a SGE Grob-type splitless injector system, a detector modified to reduce dead volume, and an HP 3390 integrator-recorder. A 25m x 0.2 mm ID, SP-2100, fused silica column was used with hydrogen as carrier gas at a linear velocity of 35 cm/sec. Two temperature programs were used: in most cases the regime was 60° to 280° at 4°/min.; however, when resolution of isoprenoid diastereomers was required, the program was 60° to 100° at 2°/min., 100° to 160° at 1°/min. then 160° to 280° at 4°/min. Levels of hydrocarbons were estimated by comparing the levels of benchmark peaks in the C_{10} to C_{30} region with those in the Tank 4 standard; alternatively, where this was not appropriate, quantitation was carried out using detector response calculations. The method sensitivity was approximately 1 ug/l in the water sample. Injection reproducibility was found to be better than ± 2%; injector fractionation was insignificant below C_{28}, but losses increased to approximately 20% at C_{32} and 60% at C_{36}. Gas chromatograms of samples containing very low levels of material showed peaks at retention times less than that of C_{12} due to volatile contaminants derived from the silicic acid.

Capillary Gas Chromatography - Mass Spectrometry (GC-MS-DS). This was carried out using a Hewlett Packard 5985B GC-MS-DS system. Chromatography conditions were identical to those described above. The mass spectrometer was operated in the E.I. mode at 70 eV.

2.2. Sample Collection

Collection of Fish for Sensory Evaluation and Chemical Analysis.

Fish were collected by netting or trawling on a number of occasions and at a variety of locations: samples described as "Outfall" were collected from the warm BPRK outfall stream using a 50 m sein from the beach. Those described as "Warnbro" were captured in Warnbro Sound approximately 10 km to the south of Cockburn Sound. Fillets were obtained from a number of fish, wrapped in clean aluminium foil, and frozen. Individual fillets were used for sensory evaluation, but in the work reported in this report, aggregates of fillets from three individual fish were used for chemical analysis.

Collection of Mussels.

On 15th July 1981, samples of mussels were collected from a bottom site in 2.5 m of water, approximately 250 m southwest of the outfall. On the same day, a control sample was collected from the far northwest extremity of the Sound at a depth of 50-100 cm on Beacon Head Dolphin.

Effluent Waters.

Water samples of 900 ml were collected periodically from streams and from the combined effluent stream in one-litre glass stoppered bottles. Dichloromethane was added directly following sampling. The combined effluent stream is not homogeneous, values to the south usually being much higher than those to the north. The precise sampling locations varied with changes in tides and sea states, and on some occasions point samples were taken whereas on other occasions samples were collected by traversing the effluent stream. Averaging the values quoted in Table 1 should however give a crude estimate of the petroleum burden of the outfall as a whole. At each time of sampling, an oil sample for use as a standard was collected from Tank 4 which accumulates the skimmings from all of the oil and water separation units. This tank is routinely pumped out at least once a day, and the oil is returned to the process stream.

Cockburn Sound Waters.

Collections of Cockburn Sound water were carried out on three occasions: 31st March, 15th July, and 16th October, 1981. At each site, seawater (3.3 l) was collected in a 3.8 l brown glass bottle at a depth of 50 cm by use of a cradle and buoy sampling

device. A number of samples were also collected 30 cm from the bottom. Dichloromethane (50 ml) was added shortly after collection. Sample sites were positioned on a time/boat speed basis for those between the BPRK outfall and the James Point Beacon; others were located by compass triangulation. In order to minimise the risk of contamination, the boat was driven towards a sample site and the motors were stopped and raised so that the boat drifted onto the station. Water samples were also collected at Beacon Head Dolphin at the northwest extremity of the Sound.

2.3 Sample Treatment

Treatment of Water Samples. On return to the laboratory, the dichloromethane layer was separated with a pipette and the water was extracted with further quantities of dichloromethane (2 x 30 ml). The extracts were dried with anhydrous sodium sulphate and the dichloromethane was then removed to leave 10 ml of solution. UV fluorescence measurements were carried out on this sample. Selected samples were then fractionated by liquid chromatography on a 6 cm x 0.6 cm silicic acid column. A saturate fraction was obtained by eluting with pentane, and an aromatic fraction was obtained by eluting with 5% ether in pentane. The aromatic fraction was concentrated to 20 ul, then it was further purified by preparative HPLC. The fraction eluted with 15% dichloromethane in hexane at 2 ml/min was collected as aromatic compounds. This material was concentrated to approximately 100-400 ul by evaporation in a stream of nitrogen at 40^{o}C, then set aside for capillary gas chromatography and GC-MS-DS studies.

Treatment of Biota Samples - Fish and Mussels. Frozen fish samples were selected for analysis on the basis of the results from sensory evaluation. Mussels were washed with water, shucked, drained to constant weight, and frozen. Flesh (100g) and KOH (100g) were weighed directly into a 500 ml flask then 70% methanol in water (200 ml) was added and this mixture was refluxed for 12 h under nitrogen, then cooled. The digest was extracted with pentane (2 x 200 ml) and the extracts were transferred into a 500 ml flask. The pentane was evaporated by warming the flask gently and KOH (50 g) and 70% methanol in water (100 ml) was added and the mixture was refluxed for a further 4 h. The digest was then extracted with pentane (2 x 100 ml). The pentane extracts were washed with water (5 x 500 ml), 1% HCl (200 ml), and again with water (2 x 500 ml), then evaporated to approximately 5 ml. The residue was applied to a 6 cm x 1 cm column of silicic acid with a short plug of anhydrous sodium sulphate on top to remove traces of water. The saturate fraction was eluted with pentane and the aromatic fraction with 5% ether in pentane and the fractions were concentrated to approximately 100 ul. The aromatic fraction was further purified by liquid chromatography in the manner described above for the water extracts. In one trial, 2,3-dimethylnaphthalene (5 ng) was added to the mixture prior to digestion; subsequent GC analysis showed that 80% of this material was retained through the treatment procedures.

3. RESULTS AND DISCUSSION

3.1 Levels of Petroleum in BPRK Effluent Streams.

Results obtained by UV fluorescence for levels of petroleum in the BPRK effluent streams are presented in Table 1. On three occasions, samples analysed by UVF were also analysed by gas chromatography: a comparison of the UVF and GC results is presented in Table 2. On approximately one occasion per week BPRK staff measure oil levels in the effluent streams using a technique involving extraction with carbon tetrachloride followed by estimation using infrared spectroscopy. Values obtained during 1981 are presented in Appendix 1 to this report. There is clearly considerable variation from time to time in the levels in each stream as one would expect with changes in refinery operations. The difficulty in obtaining a representative sample of the combined effluent stream is manifest from the values presented in Table 1. The stream is not homogeneous, petroleum levels to the south usually being much greater than those to the north. This reflects the usually greater contribution of South Outfall (and API-1) to the petroleum burden of the effluent.

Values presented in Table 1 are subject to a number of further limitations. For example, uncertainties in water flows especially relating to API-1, Sewer Box 33, and South Outfall, mean that the values quoted for quantities of petroleum are likely to be only very crude approximations. Secondly, the use of a method employing occasional random spot tests to attempt to monitor a system which is varying continuously has obvious drawbacks. Thirdly, single grab samples of dilute streams are also subject to error from fortuitous collection of an anomolous sample (chance collection of a 2-mg oil droplet would make nonsense of most of the values in Table 1 and Appendix 1). Finally, there is the matter of the analytical method. Both the IR and UVF methods require the use of a standard oil which has similar properties to the oil being analysed. This is a particularly serious consideration with UVF, as the fluorescence properties of various oils may vary by as much as factor of ten. In the present study for example, the chrysene equivalence factor for the various Tank 4 standards ranged from 3.5 to 10. On this basis, IR might therefore be considered the preferred method. On the other hand, however, the UVF method is capable of approximately two orders of magnitude greater sensitivity, and in the present study the decision was taken to use UVF so that petroleum concentrations could be followed using a single method from the Outfall out into the Sound. Capillary gas chromatography provides more information about the petroleum contaminant and is potentially less subject to interferences, but it is not as convenient a method for use in routine analysis.

Table 1: Petroleum burdens (in ug/l and kg/day) of BPRK outfalls at various dates in 1981. These were determined by UV fluorescence and are quoted in terms of a Tank 4 standard collected on the day of sampling. The concentration values can be converted into terms of chrysene equivalence by dividing by the chrysene equivalence factor.

OUTFALL AND SOURCE	FLOW IN MEGALITRES PER DAY	14 JANUARY		25 JUNE		8 JULY		15 SEPTEMBER		2 OCTOBER		8 OCTOBER		16 OCTOBER	
		ug/l	kg/d	ug/l	kg/d	ug/l	kg/d	ug/l	kg/d	ug/l	kg/d	ug/l	kg/d	ug/l	kg/day
NORTH API - 2	87	15	1	30	3	NA	NA	60 50	5	NA	NA	NA	NA	NA	NA
CENTRE Circular Separators	140	40	6	70	10	NA	NA	260 250	36	NA	NA	20	3	880	123
SOUTH API-I and Circular Separators	86	10,000	860	3,000	258	9,000 8,500	752	2,000 2,600	198	705	60	300	26	1550	133
BP NO.1 Cat. Cracker	40	8	1	30	1	NA	NA	10 10	1	NA	NA	5	NA	NA	NA
Combined Effluent Stream*	353	NA	NA	NA	NA	220 150 270 360	88	250	88	484 25	88	20m 70m 17 35 36 27 60	13	5m 1390 790	384
Chrysene Equivalence factor		NA		10		10		7		3.5		3.5		4	

* The combined effluent stream is not homogeneous and its shape and its location varies greatly with changes in tide and sea state. Excepting for the 8 July and 9 September samplings when attempts were made to obtain an averaged representative sample, samples were collected at a large number of points in the stream moving from north to south.

Table 2: Levels of petroleum in effluent waters. A comparison of UVF and GC values (ug/l)

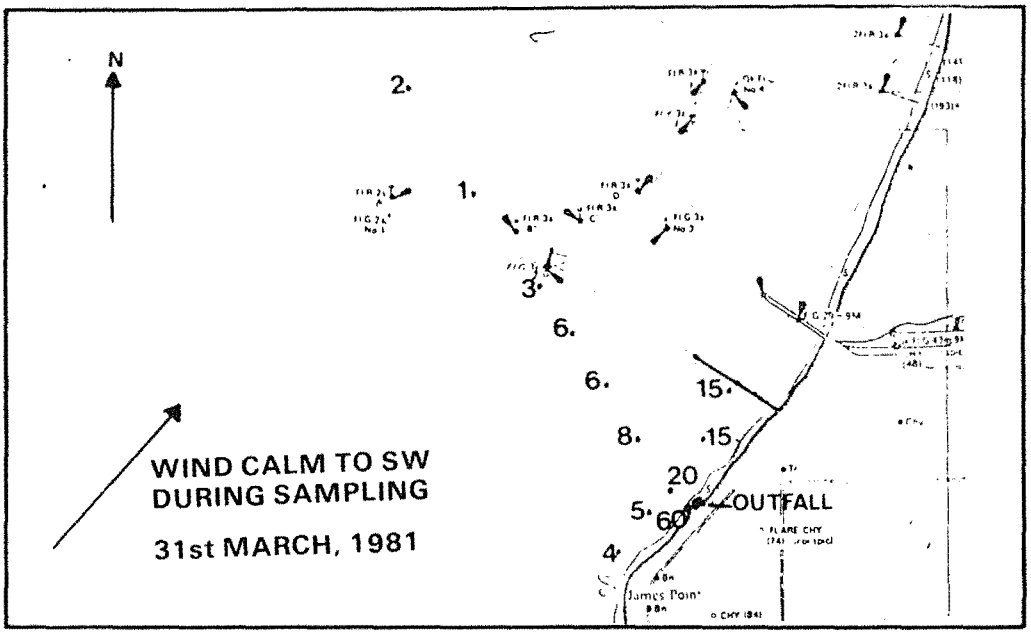
DATE	STATION NUMBER	DISTANCE FROM OUTFALL	UVF (TANK 4)	GC	
				SATURATES	AROMATICS
31 MARCH 1981	1	50 m	60	40	15
	2 (TOP)	150 m	20	25	10
	2 (BOTTOM)	150 m	12	6	2
	12	700 m	15	10	-
15 JULY 1981	COMBINED EFFLUENT STREAM		325	225	55
	9	900 m	32	27	4
	14 (BOTTOM SITE 1)	250 m	9	20	NOT DETECTABLE
16 OCTOBER 1981	SOUTH		1550	5000	700
	CENTRE		880	2200	
	COMBINED EFFLUENT STREAM (SOUTH)		790	1700	350
	1	50 m	23	15	4
	2	300 m	5	3	
	3	500 m	5	4	
	5	1000 m	2	1	
	12	750 m	9	6	
	11 (BOTTOM SITE 13)	870 m	6	8	

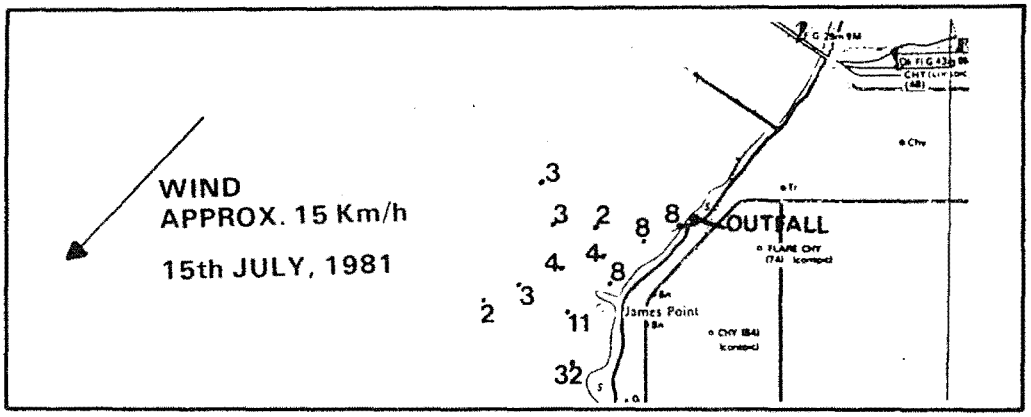
Some comparisons between values obtained for oil in effluents using both the UVF techniques and capillary gas chromatography are given in Table 2. There was very good agreement between the two techniques with the sample collected on 15th July 1981; however, the values obtained on 16th October illustrate some of the difficulties associated both with control of refinery effluents and their monitoring. When the effluent from Circular Separators was checked early in the morning by BPRK staff, it was quite clean; however, at the time of sampling we noted that it was obviously contaminated with petroleum and the analytical results confirmed this observation. As is shown in Table 2 there is a discrepancy between the petroleum levels obtained by UVF and those obtained by GC for samples collected at the outfalls and in the combined effluent stream; the GC values being higher by a factor of 2.5 to 3.5. Gas chromatograms of the saturate fractions from both Centre Outfall and South Outfall were virtually identical, strongly suggesting that a pulse of petroleum was passing through Circular Separators and being released via these two outfalls at the time of sampling, and further, that this material had a much lower level of fluorescent material than that contained in the Tank 4 standard collected at the time of sampling.

3.2 Levels of Petroleum in Cockburn Sound Waters.

Samples of Cockburn Sound waters were collected on 31st March 1981, 15th July 1981 and 16th October 1981. The results of analysis of these samples by UVF, using a Tank 4 standard collected on the same day, are presented in Figure 3. One cannot help but be struck by the apparent rapid diminution of the petroleum levels as the effluent plume moves out into the Sound. Between one and two kilometres from the Outfall, values were found to be approaching those for the background levels in the Sound. The anomolously high value of 32 ug/l in the values of 15th July may be related to the rather shallow and sheltered nature of this site. There are two major limitations inherent in the UVF method. The principal one is the fact that one uses unidentified fluorescent components of the oil, which may of course perform quite differently in the water column to other components of the oil, as a surrogate for the whole oil. There is also the possibility that refinery effluent hydrocarbons could vary in fluorescent properties over the time that the sampling is conducted. We therefore elected to analyse the fractions obtained from a suite of water samples by capillary GC: selected chromatograms of saturate fractions are presented in Figure 4. Unfortunately, this exercise was carried out using samples collected on 16th October 1981, when there was apparently a discontinuity in the composition of effluents when the samples were being collected at the Outfall. Inspection of the traces demonstrates clearly the rapidity with which hydrocarbons of increasing molecular weight are depleted with increasing distance from the Outfall.

Figure 3: Petroleum levels in Cockburn Sound waters determined by UVF (ug/l)





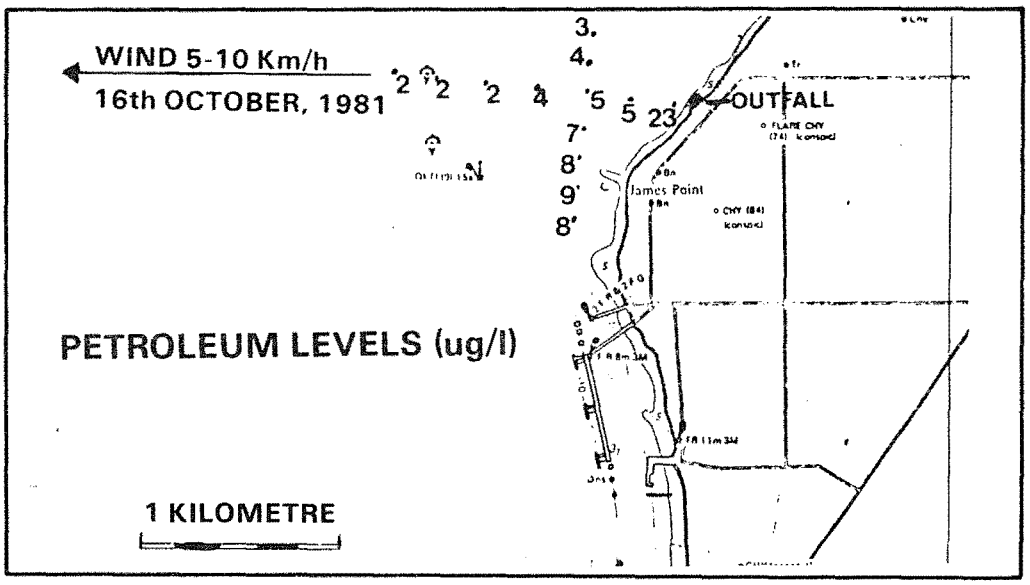
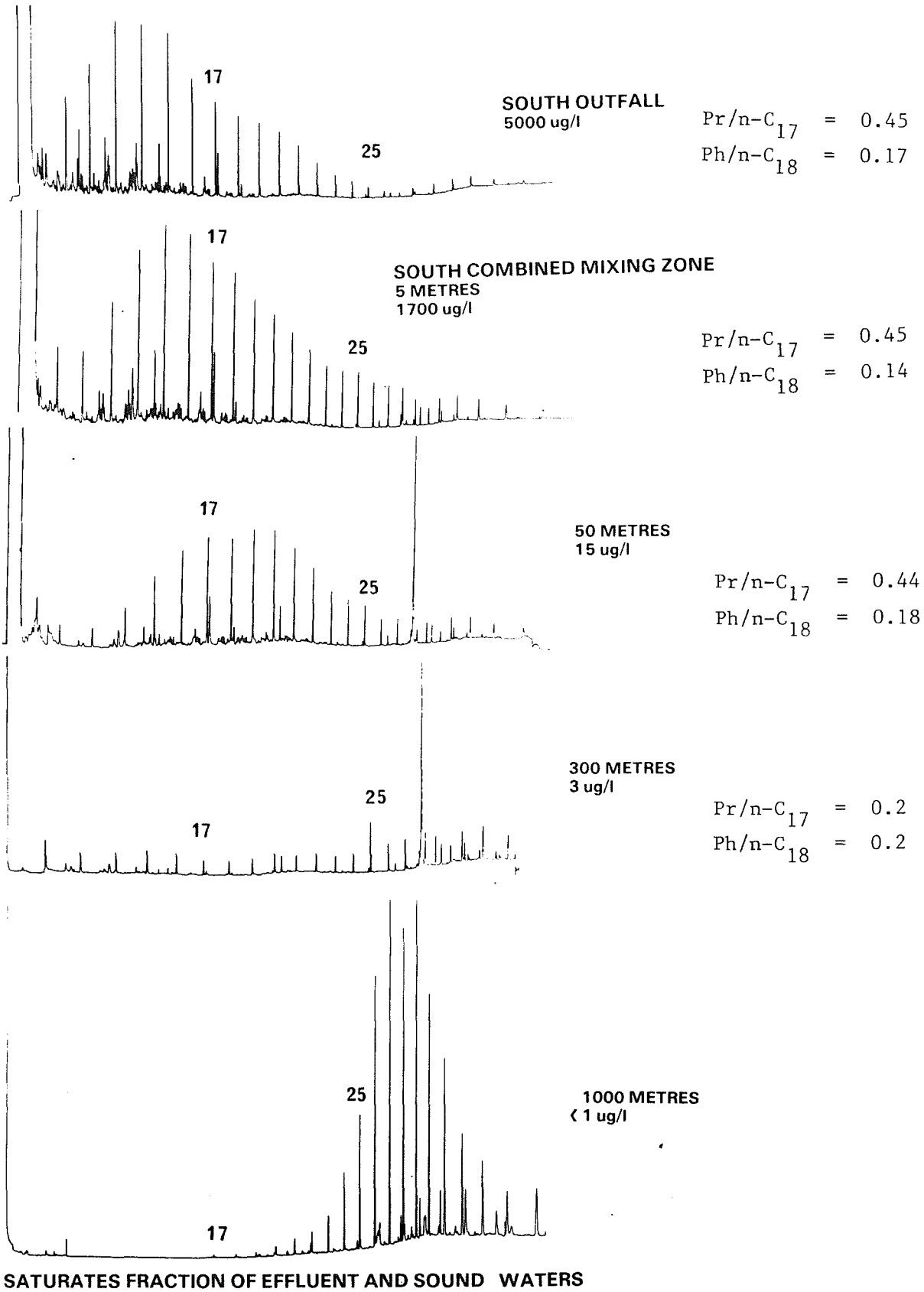


Figure 4: Capillary gas chromatograms of saturate fractions of effluent and Cockburn Sound waters collected on 16th October 1981.



SATURATES FRACTION OF EFFLUENT AND SOUND WATERS

The appearance of the n-alkanes in each chromatogram as a smooth envelope with no significant OEP suggests that the saturate fraction of the extracts is comprised largely of petrogenic material. There is also no evidence that the loss of hydrocarbon is due to weathering processes other than evaporation. Indeed, the pristane/n-C_{17} and phytane/n-C_{18} ratios are either constant or else they actually decrease, which is the reverse of the trend expected if biodegradation were playing a major role, and suggests instead that there has been a change in the initial ratios of these components in the petroleum in the effluent leaving the outfalls. Fractions of selected samples collected on 15th July 1981 were also analysed by capillary GC, and the results of all these analyses are presented in Table 2. The agreement between the UVF results and the GC results is surprising, considering the fact that the fluorescent material on the one hand and the alkanes which give rise to the gas chromatograms are probably depleted by quite different weathering processes.

3.3 Levels of Hydrocarbons in Cockburn Sound Mullet.

Yelloweye mullet (Aldrichetta forsteri) were collected from Warnbro Sound and from BPRK outfall stream, within an approximate distance of 50 m from the beach. Fillets were taken from fish and frozen: individual fillets were used for sensory evaluation trials and chemical analysis was carried out both on individual fillets and on aggregates of fillets from three individual fish. Only the latter results, using Outfall mullet adjudged as highly tainted with petroleum by the tasting panel, are presented in this report. Two sequential caustic digests were carried out to remove ester material, followed by a preliminary cleanup using a silicic acid column which gave a saturate fraction eluted with pentane. The aromatic fraction was then further purified by HPLC using a Merck Silica 60 column which had been calibrated using standard compounds. The GC traces shown in Figure 5 of the aromatic fractions of Outfall mullet, effluent water, and Warnbro mullet leave little doubt that the Outfall mullet contains substantial amounts of aromatic material; components readily identifiable by GC and GC-MS include methylnaphthalenes (MN), dimethylnaphthalenes (DMN), and trimethylnaphthalenes (TMN). The presence of other higher molecular weight aromatics was demonstrated by GC-MS (See Table 3, p 25). One might expect that if the more volatile benzenoid aromatics were present in the original sample, they would have been lost or depleted in the sample treatment procedures.

Traces of the gas chromatograms of the saturate fractions of Outfall mullet and Warnbro mullet are shown in Figure 6. At first blush, one might conclude that these simply reflect the trend shown with the aromatic fractions. That is, gross contamination of the Outfall sample with petrogenic material. Closer inspection, however, provides some illuminating insights. The increased level of odd-numbered n-alkanes over the largely petrogenic even-numbered homologues is a clue, but the true nature of the situation is revealed in the insets to Figure 6. By far

Figure 5: Capillary gas chromatograms of aromatic fractions of South Outfall water and mullet extracts.

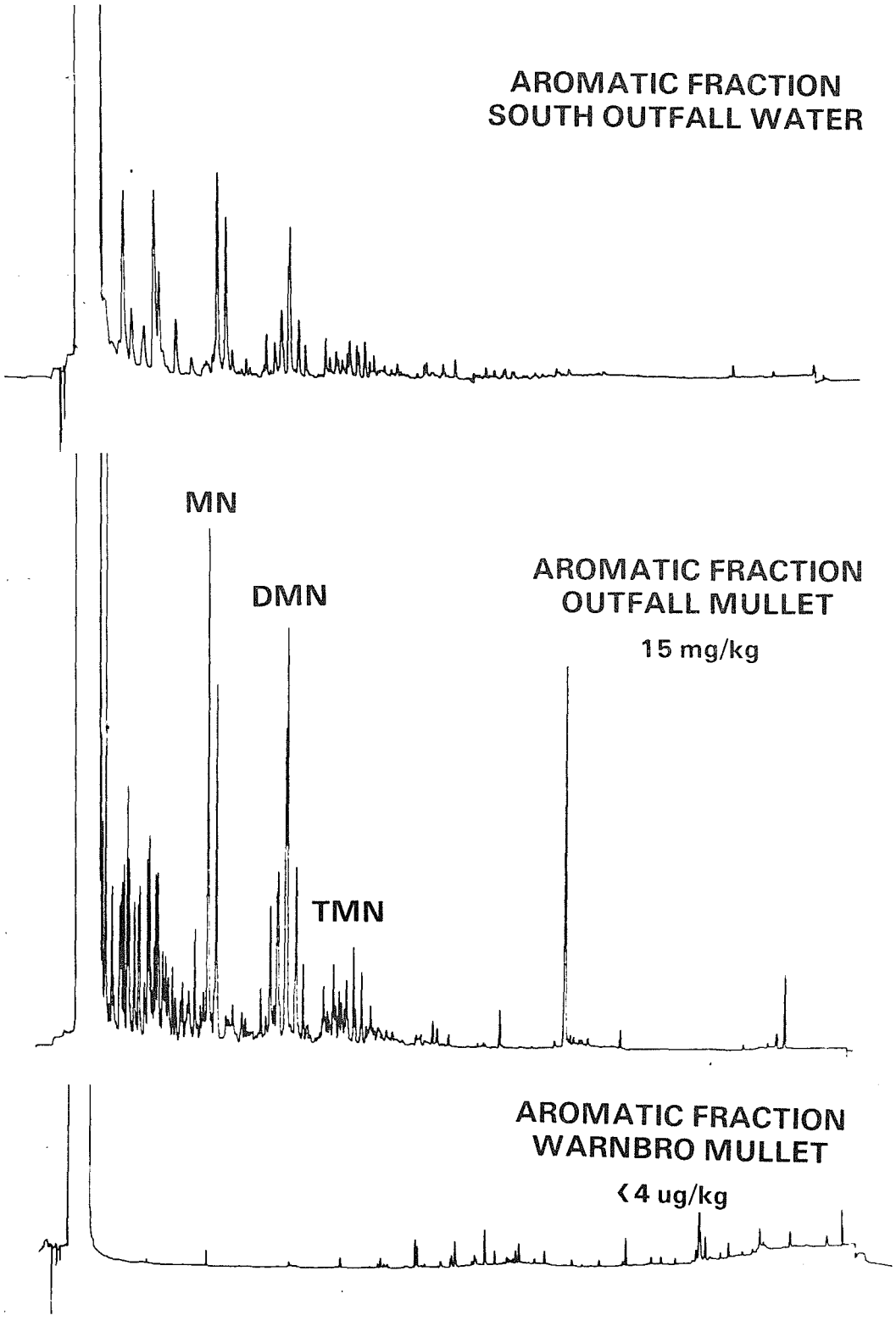
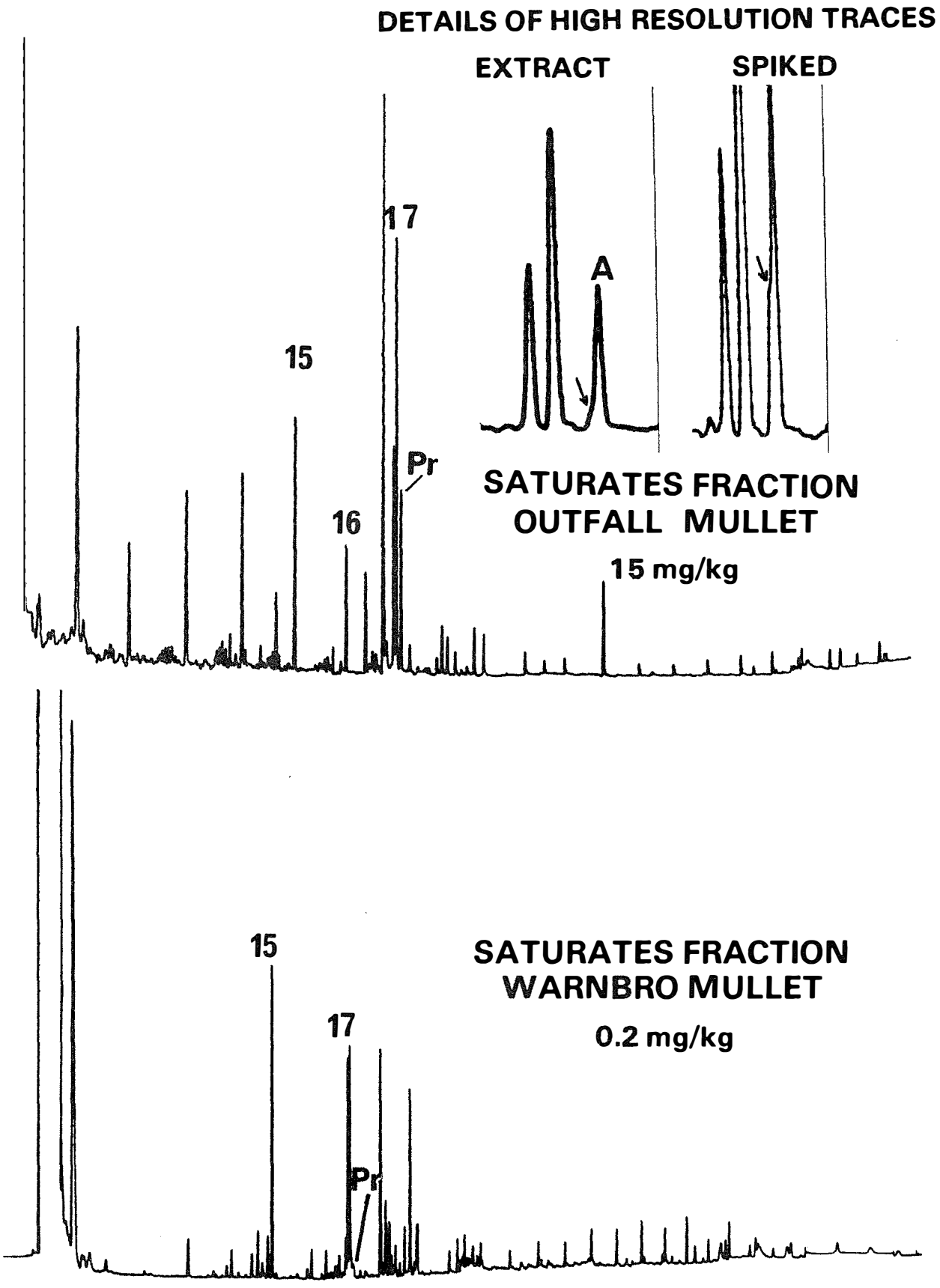


Figure 6: Capillary gas chromatograms of saturate fractions of mullet samples. Insets are high resolution chromatograms of the pristane peak of the extract (left) and the extract spiked with Table 4 standard (right).



the greatest proportion of pristane in this aggregate mullet sample is biogenic in origin. In the high resolution GC of the Outfall mullet, the peak due to pristane (A) shows only a small inflection at the front due to the petrogenic diastereomers; in the trace of the same sample spiked with alkanes from Tank 4 the peak due to petrogenic isomers is much more pronounced. The high level of biogenic hydrocarbons present in Cockburn Sound mullet suggests that the increased level of biological activity in Cockburn Sound due the nutrient-rich effluents from CSBP, KNC, and WPTP are greatly increasing the production of biogenic hydrocarbons in the Sound, and these are appearing in the fish. The enhanced levels of aromatic components in the fish suggests that these more-soluble compounds are being absorbed by fish swimming in the warm effluent waters, and that it is probably these aromatic compounds which are giving rise to the tainting problem found with fish captured in the vicinity of the Outfall.

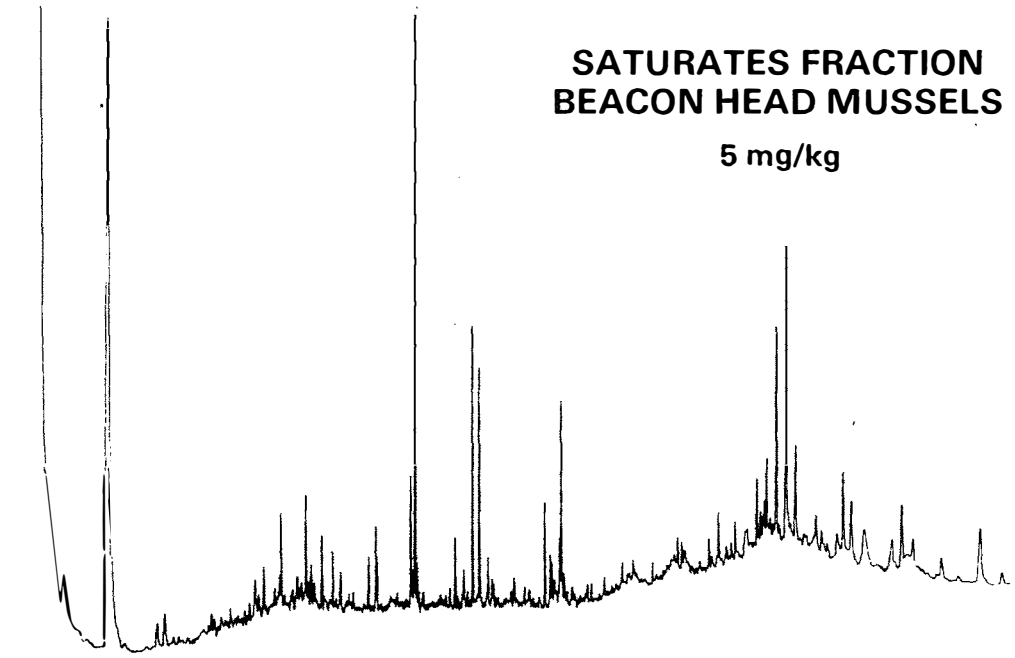
3.4 Levels of Hydrocarbons in Cockburn Sound Mussels.

At the time of the water sampling carried out on 15th July 1981, samples of mussels were collected from Beacon Head and from a bottom site approximately 250 m south-west of the outfall in water approximately 2.5 m deep. The organic extracts were fractionated into saturate and aromatic fractions by column chromatography using silicic acid as described above for the mullet samples.

Capillary gas chromatograms of saturate fractions of mussels from Beacon Head and the BPRK outfall are shown in Figure 7. These chromatograms were obtained under identical conditions and are therefore directly comparable. They show little resemblance to those of the water samples shown in Figure 4. The chromatogram of the Outfall mussels shows the typical UCM pattern characteristic of weathered petroleum, with peaks possibly due to biogenic hydrocarbons superimposed on the broad envelopes. In order to establish that the UCM was in fact hydrocarbons, the mass spectrum was examined at over a dozen points: at each point the mass spectrum showed only a pattern typical of alkanes. Estimation of the concentration of saturates in the mussels on the basis of GC detector response gave values of 50 mg/kg for the Outfall sample and 5 mg/kg for the Beacon Head sample.

The aromatic fractions obtained from column chromatography on silicic acid were further purified by HPLC. Capillary gas chromatograms of the purified aromatic fractions are shown in Figure 8. In the trace of the sample from the site 250 m south west of BPRK Outfall some petroleum aromatics are clearly recognisable, in particular the methyl-, dimethyl- and trimethylnaphthalenes, however the trace is again characterised by a broad UCM. The chromatogram for the Beacon Head mussels is quite different, showing no UCM. On the basis of detector response, the gas chromatogram of the Outfall mussel fraction indicates 5 mg/kg of material; the concentration in the Beacon Head sample calculated on a similar basis is less than 4 ug/kg of material. Both samples were subjected to further analysis by

Figure 7: Capillary gas chromatograms of saturate fractions of mussels collected at Beacon Head and at a site 250 m south-west of BPRK Outfall on 15th July 1981.



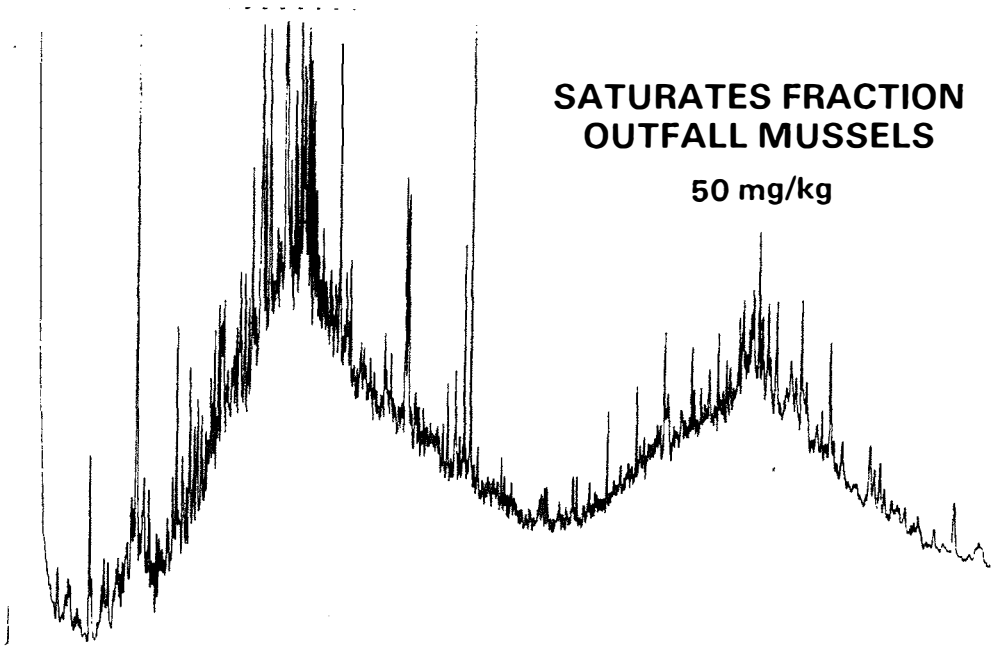


Figure 8: Capillary gas chromatograms of aromatic fractions of mussels collected at Beacon Head and at a site 250 m south west of BPRK Outfall on 15th July 1981.

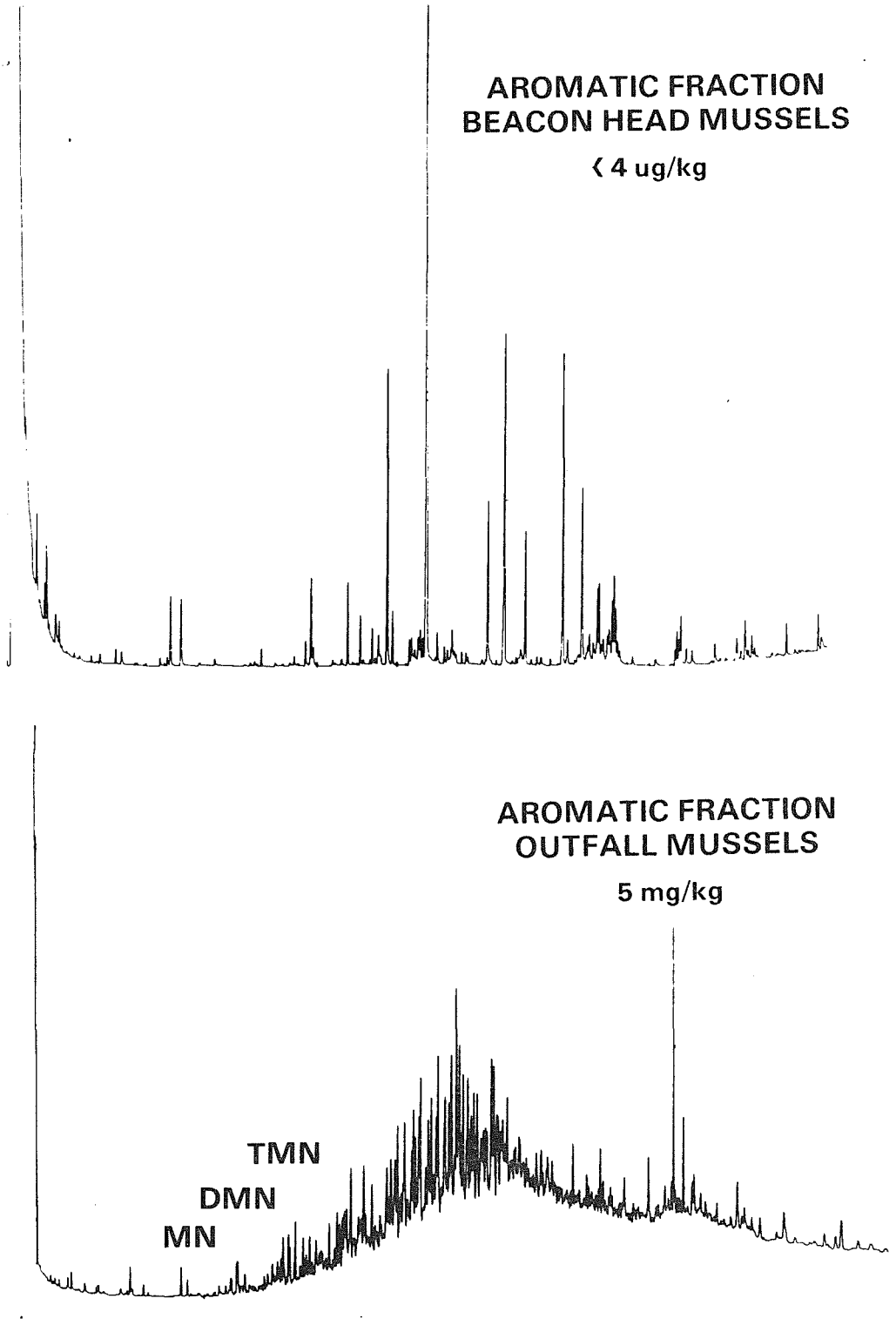


Table 3: Summary of Aromatic Compounds Determined by GC-MS in Standard, Water, Mussel, and Fish Samples.
(A blank space indicates that insufficient material was present to obtain a reliable mass spectrum.
For biota samples, using the procedures described, the detection limit is approximately 0.5 ug/kg)

	m / Z	Tank 4 Standard 15/7/81	Outfall Water 15/7/81	Outfall Mussel	Beacon Head Mussel	Untainted C.Sound Mullet	Tainted C.Sound Mullet	Untainted Sth.Beach Mullet	Tainted Sth.Beach Mullet	Untainted W.Sound Mullet	Tainted C.Sound Garfish	Untainted Sth.Beach Garfish
naphthalene	128	✓	✓	✓		✓	✓	✓	✓		✓	
methyl- dimethyl- trimethyl- naphthalenes	142 156 170	✓ ✓ ✓	✓ ✓ ✓	✓ ✓ ✓		✓ ✓ ✓	✓ ✓ ✓	✓ ✓ ✓	✓ ✓ ✓		✓ ✓ ✓	
phenanthrene	178	✓	✓	✓		✓	✓	✓	✓		✓	
methyl dimethyl- phenanthrenes	192 206	✓ ✓	✓	✓ ✓			✓ ✓	✓	✓ ✓		✓ ✓	
chrysene	228	✓		✓			✓				✓	
methyl chrysenes	242	✓										
dibenzothiophenes	184	✓	✓	✓		✓	✓	✓	✓		✓	
methyl - dimethyl - trimethyl - dibenzothiophenes	198 212 226	✓ ✓ ✓	✓ ✓	✓ ✓ ✓			✓ ✓	✓ ✓	✓ ✓		✓ ✓	
benzothiophenes	120	✓										
methyl dimethyl- trimethyl - benzothiophenes	134 148 162	✓ ✓										
pyrene	202			✓								
fluoranthene	202			✓							✓	

Table 4: Polynuclear aromatic hydrocarbons in mussels collected at a site 250 m south west of BPRK Outfall on 15th July 1981. Concentrations were calculated from mass fragmentogram peak areas.

COMPOUND	CONCENTRATION ug/kg
Naphthalene	7
Methyl naphthalenes	10
Dimethylnaphthalenes	25
Trimethylnaphthalenes	90
Phenanthrene, Anthracene	8
Methylphenanthrenes	70
Dimethylphenanthrenes	150
Chrysene	110
Perylene, Benz(α)pyrene	7
Fluoroanthene	6
Pyrene	10
TOTAL	500

GC-MS. In the case of the Beacon Head mussels, no aromatics other than the methylnaphthalene internal standard could be detected using this technique. In the case of the Outfall mussels the GC-MS data indicated that the UCM was comprised largely of derivatives of naphthalene, phenanthrene, and dibenzthiophene with from one to four carbon substituents. Specific compounds and groups of compounds identified are summarised in Table 3. Table 4 shows the concentrations of selected aromatic hydrocarbons and groups of hydrocarbons in Outfall mussels. These were calculated from mass fragmentograms using response factors determined from standard compounds.

Table 3 also contains a summary of the petroleum-derived aromatic compounds which have been identified in the various samples. From these results, it is apparent that mullet samples from Cockburn Sound and South Beach, the Outfall mussel sample and the garfish sample from Cockburn Sound all contained a range of petrogenic aromatic compounds. The samples from pristine areas used as controls, namely mussels from Beacon Head and mullet from Warnbro Sound did not contain these aromatics at concentrations above the detection limits of the instrument. Further, the garfish sample from South Beach, which was judged to be acceptable in sensory evaluation trials, did not contain detectable levels of aromatics. Finally, by way of example, the full range of aromatic compounds identified by GC-MS in the Tank 4 standard is shown in Figure 9.

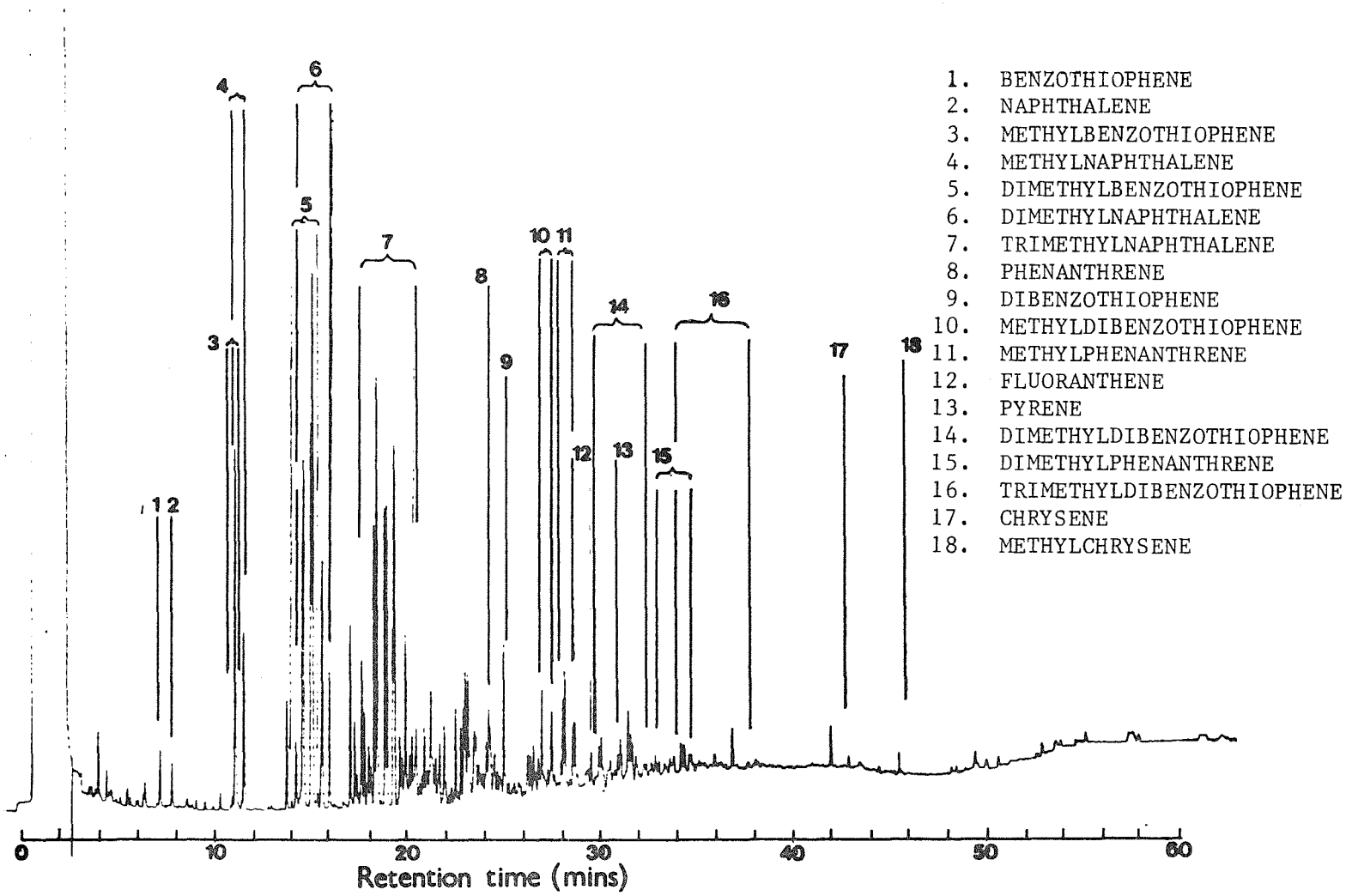


Figure 9: Gas chromatogram of the aromatic fraction from the Tank 4 standard showing peak assignments based on retention data of standard compounds and mass spectral data.

4. SENSORY EVALUATION OF FISH

4.1 Introduction

This segment of the study was conducted in collaboration with Dr. F.V. Flanagan and Ms Glenda Raymond of the Department of Home and Consumer Studies at WAIT. Collections of fish for sensory evaluation were carried out on three evenings: 8th July, 25th August, and 13th October, 1981. On the first two occasions, attempts were made to present fresh fish caught the previous evening to a large population of subjects the following day, thereby avoiding the need to freeze the samples. Partly because of difficulties in securing enough matched pairs of fish from test and control sites and partly because of other logistical problems, the steering committee elected to adopt a modified protocol for the final trials. Fish were collected, prepared for testing and stored for some days in a freezer prior to sensory evaluation by a panel of eight judges.

4.2 Sensory Evaluation Trial Number 1

4.2.1 Collection of Fish and Sample Preparation.

The first collection of fish for sensory evaluation was carried out on the 8th July, 1981. The fish were netted at night at two sites: subject fish from within 50 m of the BPRK Outfall in Cockburn Sound and control fish from South Beach, a beach just south of Fremantle approximately 20 km to the north. From each total catch, the garfish (Hyporhampus melanochir) and the yelloweye mullet (Aldrichetta forsteri Valenciennes) were selected for testing and stored on ice until filleting was carried out the following morning. Fillets of approximately 20 g were wrapped in clean aluminium foil and divided into matched pairs which were coded and stored in a refrigerator. Half were used for sensory evaluation the following day, and half were frozen and held for chemical analysis.

4.2.2 Methods.

Fillets from fifteen mullet from each of the two sites and from twelve garfish from the outfall site and eleven garfish from South Beach were used in the sensory evaluation work. Each fillet was cooked separately and without seasoning under fixed conditions for 50 seconds in a microwave oven. The questionnaire used is shown in Figure 10. Thirty five male and female subjects registered responses by placing symbols (+ or V) at the appropriate place on each scale. Each subject tested two pairs of samples (Sound mullet and Control mullet and Sound garfish and Control garfish): the order of sample presentation was random. The responses were

then scored on a fifty-point scale and paired "t" tests were conducted using the relation:

$$t = \frac{D}{S_D/\sqrt{n}}$$

D is the mean of differences of paired observations
S_D is the standard deviation of the differences
n is the number of paired observations.

The hypothesis tested was that the scores of fish from the outfall site were less than those from the control site. A one-tailed test of significance was used, and Ho was rejected if $P(t) < 0.05$.

4.2.3 Results and Discussion.

The results from Sensory Evaluation Trial No 1 are collected in Table 5 (mullet) and Table 6 (garfish). Conclusions which can be drawn from these results may be summarised as follows

1) Compared with the control samples collected at South Beach, both garfish and mullet caught within 50 m of the beach at BPRK Outfall were judged to be much less acceptable, having flavours which were less pleasant, unusual, and oily. These effects were more apparent with the garfish than the mullet. Further, the results show that unpleasant aftertastes and increased flavour strength were more apparent with the garfish samples. These differences perhaps might reflect the stronger natural flavours and greater oiliness of the mullet, or the more marked surface swimming behaviour of garfish.

2) There were no negative effects on the texture of either variety, but there were signs that the colour of the mullet may have been adversely affected to a slight extent.

3) Many respondents commented upon the presence of petroleum type flavours (rubber, kero, peculiar, chemicals, etc) in the Sound sample in particular. These comments were so negative that, when relayed back to other potential tasters, there was a high refusal rate.

4) There were some signs that certain fillets were more adversely affected than others, and even the possibility that some fish caught outside the Sound were also contaminated.

4.3 Sensory Evaluation Trial Number 2

4.3.1 Collection of Fish and Sample Preparation.

The second collection of fish for sensory evaluation was carried out on 25th August 1981. On this occasion fish were netted at night from four locations: control fish from South Beach, and test fish from within 50 m of BPRK Outfall and from sites approximately 500 m south and north of BPRK Outfall. Unfortunately, the species represented in the catch tended to be grouped at each sampling site so that it was difficult to select matched species pairs from control sites and from tests sites. Yelloweye mullet (Aldrichetta forsteri Valenciennes) and Perth Herring (Nematalosa vlaminghi Munro) were chosen as the fish for testing and treated in the manner described for the first trial, with the exception of course that much greater numbers of smaller fillets (approximately 5 g) had to be taken from individual fish for sensory evaluation. No fillets were available for preservation for chemical analysis. The numbers of fish collected at each site and the numbers of fillets from taken from each fish are set out in Table 7.

4.3.2 Methods

The food preparation and sensory evaluation measurement techniques used were similar to those reported for Trial Number 1. Each subject tasted three samples presented in random order: twenty nine respondents evaluated herring fillets and thirty one different respondents evaluated mullet fillets. For each fish variety three paired "t" tests were conducted using the scores on each attribute in a manner directly analogous to that described for Trial Number 1.

4.3.3 Results and Discussion.

The means and standard deviations of the scores and the results of the statistical comparisons on each attribute are collected in Table 8 (herring) and Table 9 (mullet).

Herring

On the attributes which may be construed as indicators of tainting (acceptability, oily flavour, unusual flavours and aftertaste overall pleasantness) herring from the sites 500 m to the north or to the south of BPRK Outfall were significantly less acceptable than the control sample. No significant differences were detected between samples from the north and south sites.

Figure 10: Questionnaire used for sensory evaluation trials.

Codes +C_____ M _____
W
VS_____ M _____
W

FISH EVALUATION Name:_____

Type _____ Date:_____

Please test the fish in the order nominated by the experimenter.
Place symbol at appropriate place on each scale.

FLESH COLOUR

Very unpleasant Very pleasant
I.... I

TEXTURE

Very unpleasant Very pleasant
I.... I

FLAVOUR PLEASANTNESS

Very unpleasant Very pleasant
I.... I

FLAVOUR STRENGTH

Very unpleasant Very pleasant
I.... I

UNUSUAL FLAVOURS

Very unpleasant Very pleasant
I.... I

"OILY" FLAVOURS

Very unpleasant Very pleasant
I.... I

AFTER TASTE

Very unpleasant Very pleasant
I.... I

OVERALL ACCEPTABILITY

Totally unacceptable Totally acceptable
I.... I

COMMENTS:_____

_____

Table 5: Results from Sensory Evaluation Trial No 1: mullet from BPRK Outfall and South Beach Control

Attribute	Sample Location	Mean	S.D.	t-value	P(t)	Comments and Conclusions from Statistical Comparisons
Overall Acceptability	Outfall	15.7	13.2	2.14	0.039	Outfall samples less acceptable than Control
	Control	21.9	11.0			
Oily flavours	Outfall	25.3	16.2	3.67	0.001	Outfall samples much more oily than Control
	Control	14.9	12.2			
Unusual flavours	Outfall	28.4	15.4	3.87	0.001	Outfall samples had more unusual flavours than Control
	Control	17.2	11.6			
Flavour strength	Outfall	30.2	12.5	2.06	0.046	Outfall samples slightly more strongly flavoured than Control
	Control	25.2	11.2			
Aftertaste pleasantness	Outfall	17.9	13.2	1.48	0.148	Aftertaste pleasantness difference not statistically significant
	Control	22.0	9.5			
Flavour pleasantness	Outfall	16.5	13.0	2.17	0.036	Outfall samples slightly less pleasant than Control
	Control	22.3	12.2			
Flesh Colour pleasantness	Outfall	19.6	9.5	2.19	0.034	Colour of Outfall samples slightly less pleasant than Control
	Control	23.3	8.5			
Flesh texture pleasantness	Outfall	20.6	10.8	1.3	0.202	No difference in textures
	Control	23.6	10.7			

Table 6: Results from Sensory Evaluation Trial No 1: garfish from BPRK Outfall and South Beach Control

Attribute	Sample Location	Mean	S.D.	t-value	P(t)	Comments and Conclusions from Statistical Comparisons
Overall Acceptability	Outfall	10.7	9.6	6.9	0.000	Control was acceptable but the majority of subjects judged Outfall garfish to be unacceptable
	Control	27.6	12.1			
Oily flavours	Outfall	29.0	16.1	5.05	0.000	Compared with Control, Outfall samples profoundly oil tainted
	Control	13.6	10.9			
Unusual flavours	Outfall	33.3	14.6	5.74	0.000	Flavour of Outfall samples most unusual compared with Control
	Control	14.0	10.5			
Flavour strength	Outfall	32.8	14.6	3.65	0.001	Outfall sample tastes stronger than Control
	Control	22.0	10.1			
Aftertaste pleasantness	Outfall	15.8	13.1	3.16	0.004	Control was satisfactory, but Outfall sample had unpleasant aftertaste
	Control	25.3	12.2			
Flavour pleasantness	Outfall	13.3	11.0	5.2	0.000	Control was satisfactory; Outfall sample profoundly unpleasant
	Control	25.4	11.7			
Flesh Colour pleasantness	Outfall	30.1	11.8	1.07	0.29	No significant difference perceived
	Control	27.2	11.1			
Flesh Texture pleasantness	Outfall	26.1	11.1	0.94	0.35	No significant difference perceived
	Control	27.7	11.6			

Table 7: Fish Collected for Sensory Evaluation Trial Number 2

	Location	Number of fish	Number of fillets from individual fish
Mullet	South Beach	3	12, 16, 3
	BPRK Outfall	3	17, 7, 7
	500 m south of Outfall	4	5, 10, 7, 9
Herring	South Beach	2	14, 15
	500 m south of Outfall	4	7, 8, 7, 7
	500 m north of Outfall	4	7, 8, 7, 7

Mullet

The situation with the mullet is much less clear, many of the results being quite contradictory. For example, no significant differences were found in the attributes oily flavours and flavour strength. On the attributes overall acceptability, unusual flavours, and aftertaste pleasantness, fish from the site 500 m from the Outfall scored more poorly than both those from the control site and from the outfall site.

Using the procedures adopted in this trial, one can draw only very limited conclusions from the results. Firstly, herring from sites 500 m to the north and south of BPRK outfall showed indications of tainting with petroleum compared with the control sample from South Beach. Secondly, there were some indications that mullet from the site 500 m to the north of BPRK Outfall were tainted, but the results are far from conclusive. The principal outcome of this trial was that it focussed attention upon the limitations implicit in using very small numbers of fish in the tasting experiments: chance collection of atypical fish at either control or test sites can drastically distort the results, particularly if, as was the case with the mullet samples, different numbers of fillets are taken from individual fish. These observations led the Steering Committee to abandon the attempt to test unfrozen fish, and to adopt a revised experimental procedure.

Table 8: Results from Sensory Evaluation Trial Number 2: herring from the control site at South Beach, and from sites 500 m to the north and south of BPRK Outfall

Attribute	Sample Location	Mean	S.D.	Comments and Conclusions from Statistical Comparisons
Overall acceptability	Control	30.0	14.4	North and South similar and significantly less acceptable than control
	North	17.8	13.1	
	South	20.9	12.4	
Oily flavours	Control	12.4	10.3	North and South similar and significantly more oily flavours than Control
	North	24.1	13.6	
	South	22.6	13.6	
Unusual flavours	Control	13.6	11.9	North and South similar and significantly more unusual flavours than Control
	North	27.7	14.3	
	South	22.5	13.9	
Flavour strength	Control	25.8	13.6	North has stronger flavour than Control: other differences not significant
	North	31.2	11.2	
	South	29.0	10.3	
Aftertaste pleasantness	Control	29.7	13.8	Control has more pleasant aftertaste than North and South samples
	North	17.8	12.7	
	South	22.0	11.5	
Flavour pleasantness	Control	30.0	13.5	Control has more pleasant flavour than North and South samples
	North	17.8	13.3	
	South	21.5	10.8	
Flesh colour pleasantness	Control	31.4	12.4	Control has more pleasant flesh colour than South sample
	North	28.0	9.0	
	South	24.0	11.9	
Flesh texture Pleasantness	Control	29.8	13.6	No significant differences
	North	26.5	13.8	
	South	28.0	13.1	

Table 9: Results from Sensory Evaluation Trial Number 2: mullet from the control site at South Beach, from BPRK Outfall, and from a site 500m to the south of BPRK Outfall

Attribute	Sample Location	Mean	S.D.	Comments and Conclusions from statistical comparisons
Overall acceptability	Control	22.9	11.8	Outfall and Control similar, and both better than southern site
	Outfall	20.3	13.7	
	South	15.9	13.0	
Oily flavours	Control	20.0	12.8	All similar
	Outfall	21.3	14.7	
	South	22.5	14.8	
Unusual flavours	Control	19.8	14.2	Outfall and South similar and both have more unusual flavours than the Control
	Outfall	26.8	13.7	
	South	29.8	14.8	
Flavour strength	Control	29.0	12.2	All similar
	Outfall	30.4	9.9	
	South	29.5	13.6	
Aftertaste pleasantness	Control	23.5	12.2	Control has more pleasant aftertaste than South; other differences not significant
	Outfall	19.4	11.9	
	South	16.0	11.9	
Flavour pleasantness	Control	22.0	10.4	Control flavour more pleasant than South; other differences not significant
	Outfall	19.9	13.3	
	South	15.7	13.0	
Flesh colour	Control	22.4	13.3	Outfall and South are similar, and both have a less pleasant colour than the Control
	Outfall	29.9	10.7	
	South	27.4	12.0	
Flesh texture	Control	23.4	11.9	All similar
	Outfall	24.1	12.6	
	South	22.5	12.8	

4.4 Sensory Evaluation Trial Number 3

4.4.1 Collection of Fish and Sample Preparation.

Whiting (Sillago spp.) were collected by netting on the evening of 13th October 1981 at the following sites: Warnbro (7 fish), BPRK Outfall (6 fish), and from locations the following distances along the effluent plume: 1 km (5 fish), 2 km (5 fish), 3 km (5 fish), 5 km (7 fish). Two large fillets were taken from each fish, wrapped in clean aluminium foil and stored in a freezer.

4.4.2 Methods.

Sensory evaluation trials were carried out early in the week following the collection of the fish. Eight small portions of each fillet were cooked unseasoned in a petri dish for 50 seconds. These samples were presented unidentified to a panel of eight judges each of whom evaluated the sample as tainted, suspect, or not tainted. A group score was then obtained, free discussion followed, and comments were recorded. After the group discussion, the identity of the sample was recorded. The bulk of the testing was carried out in one session of approximately two hours, however the samples from BPRK Outfall were tested the following day.

4.4.3 Results and Discussion

The aggregate scores for each location are presented in Table 10. It would appear from these results that any tainting of the whiting samples collected at distances 1 km or more from the outfall is comparatively minor. The evaluation of the whiting collected within approximately 50 m of the BPRK outfall, when taken together with the taint descriptions (75% of the tainted flavours were described as "petrol", "hydrocarbons" "oily" or even "outfall smell" by judges familiar with the odour of the BPRK outfall) established quite unequivocally that the BPRK outfall causes tainting of fish in the immediate vicinity. These results suggest that this testing procedure could be readily adapted to map the extent of the occurrence of tainting in the Sound in the vicinity of the BPRK outfall. It would probably not be wise, however, to include similar "Outfall" samples in the testing program for two reasons. Firstly, the strength of the flavour makes the subsequent tasting of samples with more subtle flavours a difficult matter. Secondly, the promise of such samples makes the recruitment of a suitable panel practically impossible.

Table 10: Aggregate scores of Whiting from Sensory Evaluation Trial Number 3

Sample Location#	Numbers of Samples	Tainted	Suspect	Not Tainted
Outfall	48	86%	10%	4%
1km	40	2%	20%	78%
2km	40	0	15%	85%
3km	40	0	15%	85%
5km	56	2%	7%	91%
Warnbro	56	2%	9%	89%

Distances quoted in this column refer to distance from the BPRK outfall in the direction taken by the effluent plume.

4.5 Sensory Evaluation Trial Number 4

4.5.1 Collection of Fish and Sample Preparation.

Perth Herring (Nematalosa vlaminghi Munro) were collected by netting on the evening of 13th October, 1981 in Warnbro Sound (5 fish) and at BPRK outfall (6 fish). On the same occasion six yelloweye mullet (Aldrichetta forsteri Valenciennes) were collected at BPRK Outfall. Subsequently, on 14th October, 1981, seven mullet were obtained by netting at Soldiers Cove in the Mandurah estuary, approximately 40 km to the south of Cockburn Sound. Samples of fillets were taken and stored in aluminium foil in the manner described in Trial Number 3.

4.5.2 Method.

Sensory evaluation trials were carried out as described in Sensory Evaluation Trial Number 3. The trial was carried out on the second day of testing, immediately following the completion of the remaining samples from Trial 3 (mainly Outfall samples). In order to test the reliability of the evaluations, the samples presented included duplicates of two samples tested on the first day.

4.5.3 Results and Discussion.

Herring.

The aggregate results from herring evaluations are presented in Table 11. Taken together with comments such as "petrol" and "oily" made by the panel for over 30% of the tainted samples from BPRK Outfall, these results confirm that a very high proportion of fish in the vicinity of BPRK outfall are tainted. The "tainted" and "suspect" scores of the Warnbro Sound herring totalling 30% were not associated with such comments, and rather might be attributed to some members of the panel not being familiar with the typical taste of herring.

Table 11: Sensory Evaluation Trial Number 4: Herring

Sample Location	Number of Samples	Tainted	Suspect	Not Tainted
Warnbro Sound	40	5%	25%	70%
BPRK Outfall	48	69%	18%	13%

Mullet.

The aggregate results from mullet evaluations are presented in Table 12. The results here are not as clear cut as they are for the herring samples: although 90% of judgements of the Outfall samples were again "tainted" or "suspect", in this case 57% of the Mandurah judgements were also "tainted" or "suspect". This confounding factor was to some extent overcome by the comments of the panel: nearly all comments describing the tainting of the Outfall samples alluded to petroleum. Only 10% of such descriptions were used for Mandurah samples: most described the samples as muddy, dirty, bitter, or oily.

Table 12: Sensory Evaluation Trial Number 4: mullet

Location	Numbers of Samples	Tainted	Suspect	Not Tainted
Mandurah estuary	56	34%	23%	43%
BPRK Outfall	48	75%	15%	10%

4.6 Assessment of Panel Reliability

Duplicate samples were presented on each of the two days of Sensory Evaluation Trials 3 and 4. From the results presented in Table 13, it can be seen that the panel reliability was fair to good. Indeed the Mandurah mullet sample was a very tough test as it had an ill-defined off-taste.

Table 13: Results from evaluations of identical fillets made on consecutive days to assess reliability of the judgements made

		Tainted	Suspect	Not Tainted
Mandurah Mullet	Day 1	3	3	2
	Day 2	5	1	2
Warnbro Whiting	Day 1	0	2	6
	Day 2	0	0	8

5. THE CHEMICAL BASIS OF TAINTING OF FISH CAPTURED AT BPRK OUTFALL

The gas chromatograms shown in Figure 5 and Figure 6 demonstrate clearly that aggregates of fish (in this case mullet) adjudged to be tainted contained levels of petroleum hydrocarbons which were elevated compared with those of fish from uncontaminated areas. The distributions of aromatics shown in Figure 5 for water from South Outfall and the aggregated mullet sample are strikingly similar, and are characteristic of many crude petroleums. Based upon the appearance of the n-alkane envelope (smooth, but with enhanced levels of C_{15} and C_{17}) and the high proportion of petrogenic pristane, the saturate fraction from the mullet appears to be a mixture of petrogenic and biogenic alkanes. That the tainting of these fish is due to petroleum is therefore supported by strong circumstantial evidence.

Because petroleum is such a complex mixture, a simple experiment was carried out to provide more information about the likely cause of the tainting observed in the Outfall fish. Each of the hydrocarbons shown in Table 14 was dispersed in water at a level of 10 mg/l, and the taste and odour was noted by the principal author of this report. The results are noted in the table; further, the taste of the water containing aromatic hydrocarbons was strongly reminiscent of the taste of tainted fish. These results suggest that the tainting of the Outfall fish is due, in part at least, to the volatile one- and two-ring aromatics in the BPRK effluent. If more conclusive evidence is required, this could be obtained by addition of these compound types to fish evaluated in any future organoleptic testing studies.

Table 14: Tastes and Odours of Selected Hydrocarbons at 10 mg/l in water.

Compound	Odour	Taste
Octane	Bland flat odour	None discernable
Decalin	Characteristic sharp odour	None discernable
Xylene mixture (AR) dimethylnaphthalene mixture) 1-methylnaphthalene	Characteristic, faintly sweet odour	Persistent sweet taste not unlike petrol or kerosene
Tetralin	Faintly sweet odour, similar to other aromatics) with notes similar to decalin	

6. CONCLUSIONS

Each of the aims of the study has been achieved. In so far as this is possible, the highly variable levels of petroleum hydrocarbons in each of the four BPRK Outfalls have been measured on a number of occasions, and the petroleum in the effluent stream has been characterised by gas chromatography and GC-MS. Values obtained for concentrations in the streams are in substantial agreement with those obtained by BPRK staff in their routine sampling programing; however, attention is focussed on the need to obtain more reliable information about refinery water flows before any reliable information about petroleum burdens in the effluent system can be established. Levels of hydrocarbons in the effluent plume are usually approaching those of the background (approximately 1 ug/l) in the region 1000-2000 m from the Outfall. A large proportion of the more volatile components of petroleum released into the Sound is quite rapidly lost by evaporation into the atmosphere, and less volatile material is removed by adsorption and sedimentation. Mussels collected 250 m from the outfall contain elevated levels of the more persistent branched and cyclic petrogenic alkanes (approximately 50 ppm) and higher molecular weight aromatics (approximately 5 ppm), especially alkylated naphthalenes, dibenzthiophenes, and phenanthrenes. There is strong evidence that a substantial proportion of fish captured within approximately 50 m of the beach at BPRK Outfall and adjudged as tainted in sensory evaluation trials contained elevated levels both of petroleum saturates and petroleum aromatics similar to those found in the effluent waters. The observed tainting is very likely due at least in part to the presence of one- and two-ring aromatics in the BPRK effluent stream. The evidence presently to hand does not however clearly define the extent of the occurence of fish tainting in the open waters of the Sound: indications are that only a small proportion of fish captured more than 1 km from the outfall are likely to be tainted. It would appear that the specialist panel technique developed by Dr Flannigan could provide a more precise definition of the extent of the affected zone should this be required. Reduction of the incidence of tainting of fish exposed to the BPRK effluents would appear to require a reduction in the amounts of one- and two-ring aromatics in the effluent stream. Because these compounds, which are also probably the most toxic components of petroleum, are quite volatile, a number of management options are available to effect this reduction. Consideration of these is however beyond the scope of the terms of reference of this study.

Cockburn Sound represents an interesting and complex problem in environmental science which is still unfolding as industry continues to upgrade its effluent disposal practices.

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APPENDIX 1

Weekly Summary of Petroleum Burdens in BPRK Effluent Determined on a Daily Basis by BPRK Staff Using Solvent Extraction and Analysis by Infrared Spectroscopy.

APPENDIX 1

WEEKLY SUMMARY

OIL IN EFFLUENT

Inlet Flume	mg/l / Kg/day — Week Ending	NORTH	CENTRE	SOUTH	FCCU	TOTAL	API No. 1	Number Exceeding Target
	Target	1.2 / 105	1.1 / 150	2.7 / 235	0.2 / 10	1.4 / 500	18 / 110	
N.D.	11 Jan 81	0.6 / 52.2	1.0 / 140	5.1 / 449	0.4 / 16.8	1.8 / 658	40 / 240	1
N.D.	18 Jan 81	1.2 / 105	1.3 / 182	27.2 / 2394	0.4 / 16.8	7.8 / 2696	10.1 / 60.6	2
N.D.	25 Jan 81	<0.1 / 8.7	0.2 / 28	2.2 / 194	<0.1 / 4.2	0.6 / 235	10.8 / 64.8	2
0.1 / 45	1 Feb 81	0.5 / 43.5	2.5 / 350	2.1 / 184.8	.3 / 12.6	1.6 / 580.9	Public / Holiday	3
0.4 / 172	8 Feb 81	0.4 / 34.8	0.5 / 70	0.9 / 79.2	0.4 / 16.8	0.6 / 200.8	12 / 72	3
0.4 / 172	22 Feb 81	0.4 / 34.8	0.6 / 84	2.9 / 255.9	0.4 / 16.8	1.1 / 392	42 / 252	3
<0.1 / 45	1 Mar 81	0.3 / 26.1	0.5 / 70	8.1 / 712.8	0.1 / 42	2.4 / 850.9	49 / 294	4
<0.1 / 45	8 Mar 81	0.1 / 8.7	0.2 / 28	1.6 / 139.2	0.3 / 12.6	0.5 / 188.5	93.1 / 558.6	4
<0.1 / 45	15 Mar 81	<0.1 / 8.8	0.1 / 14	3.1 / 269.7	<0.1 / 4.2	0.8 / 296.7	54 / 324	4
<0.1 / 45	22 Mar 81	<0.1 / 8.7	<0.1 / 14	1.1 / 95.7	0.1 / 4.2	0.3 / 122.6	23 / 138	4
<0.1 / 43.1	29 Mar 81	0.5 / 43.5	0.8 / 112	2.2 / 193.6	0.4 / 16.8	19 / 323	36.8 / 220.8	4
0.4 / 172.4	5 Apr 81	0.3 / 26.4	0.6 / 84	2.7 / 237.6	0.3 / 12.6	0.5 / 188.2	28.9 / 173.4	4
0.5 / 215.5	12 Apr 81	0.7 / 61	0.5 / 70	3.2 / 281.6	0.4 / 16.8	0.6 / 213.8		4
0.5 / 215.5	26 Apr 81	0.5 / 43.5	0.5 / 70	2.7 / 237.6	0.5 / 21	0.4 / 156.6		
0.5 / 215.5	10 May 81	0.4 / 35	0.4 / 54.5	4.4 / 383	0.4 / 20	0.8 / 277	24.2 / 147.8	4
<0.1 / 45.1	17 May 81	0.3 / 26	0.1 / 13.6	0.4 / 34.8	0.1 / 5	0.1 / 34.3	*	4
<0.1 / 45.1	24 May 81	0.5 / 43.8	<0.1 / 14	0.4 / 34.8	<0.1 / 4.2	0.1 / 51.7	*	4
0.5 / 215.5	31 May 81	0.8 / 70	0.2 / 27	4.7 / 409	0.5 / 25	0.9 / 315.5	66.5 / 406.3	4
0.2 / 86.2	12 June 81	0.6 / 52.2	*	1.7 / 149.6	0.3 / 12.0	*	26.8 / 160.8	*
<0.1 / 45.1	19 June 81	0.4 / 35	0.2 / 28	4.4 / 387.2	<0.1 / 4.2	1.1 / 409	28.6 / 172	4
<0.1 / 45.1	3 July 81	0.2 / 17	0.1 / 14	22.2 / 1953.6	<0.1 / 4.2	5.44 / 1943.7	23 / 138	5
<0.1 / 45.1	10 July 81	0.2 / 17	<0.1 / 14	6.1 / 536.8	0.1 / 4.2	1.6 / 527	87.3 / 523.8	6

APPENDIX 1 (Cont'd) WEEKLY SUMMARY

OIL IN EFFLUENT

Inlet Flume	mg/l / Kg/day — Target / Week Ending	NORTH	CENTRE	SOUTH	FCCU	TOTAL	API No. 1	Number Exceeding Target
		1.2 / 105	1.1 / 150	2.7 / 235	0.2 / 10	1.4 / 500	18 / 110	
0.6 / 270.6	17 July 81	2.4 / 208.8	0.5 / 70	6.8 / 598.4	0.3 / 12.6	1.73 / 619.2	39.0 / 234	7
<0.1 / 45.1	24 July 81	<0.1 / 8.7	0.1 / 14	3.7 / 325.6	<0.1 / 4.2	0.9 / 325.5	45.5 / 273	7
0.1 / 45.1	31 July 81	0.2 / 17	0.5 / 70	4.5 / 396	0.1 / 4.2	1.2 / 442.1	36 / 216	7
0.1 / 45.1	7 Aug 81	0.1 / 8.7	0.2 / 28	2.2 / 196.6	<0.1 / 4.2	0.5 / 192.4	21.4 / 128.4	7
0.1 / 45.1	13 Aug 81	0.1 / 8.7	<0.1 / 4.2	6.8 / 598.4	<0.1 / 4.2	1.6 / 570.4	65.5 / 393.0	8
<0.1 / 45.1	20 Aug 81	<0.1 / 8.7	<0.1 / 14	4.8 / 422.4	<0.1 / 4.2	1.4 / 404.2	37 / 222	8
<0.1 / 45.1	27 Aug 81	<0.1 / 8.7	0.8 / 112	2.5 / 220	<0.1 / 4.2	0.8 / 299.8	22.6 / 135.6	8
<0.1 / 45.1	11 Sept 81	0.5 / 43.5	1.6 / 224	10.1 / 888.8	<0.1 / 4.2	3.1 / 1115.5	12.0 / 72	9
<0.1 / 45.1	18 Sept 81	0.5 / 43.5	1.1 / 154	3.0 / 264	<0.1 / 4.2	1.2 / 421	27 / 162	9
<0.1 / 45.1	25 Sept 81	0.1 / 8.8	0.1 / 14.0	1.9 / 167.2	<0.1 / 4.2	0.4 / 149.1	10.6 / 63.6	9
<0.1 / 45.1	2 Oct 81	<0.1 / 8.7	<0.1 / 14.0	2.6 / 228.8	<0.1 / 4.2	0.6 / 210.6	69 / 414	9
<0.1 / 43.1	13 Oct 81	0.4 / 34.8	0.9 / 126	6.1 / 536.8	<0.1 / 4.2	1.8 / 656.7	61 / 366	10
<0.1 / 45.1	20 Oct 81	0.8 / 69.6	N/D	5.4 / 469.8	<0.1 / 4.2	* / *	38 / 228	11
<0.1 / 45.1	27 Oct 81	2.1 / 182	4.8 / 672	8.4 / 739	0.2 / 8.4	4.4 / 1556	65 / 390	12
<0.1 / 45.1	3 Nov 81	1.4 / 121.8	3.7 / 518	6.4 / 563	<0.1 / 4.2	/ 1161	40 / 240	13
<0.1 / 45.1	20 Nov	0.2 / 17.4	1.3 / 182	4.6 / 404	<0.1 / 4.2	1.5 / 552.5	24.1 / 144.6	14