

Crude Oil Derived Petroleum
Products in the Aquatic
Environment:
Priorities for Control

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R&D Technical Report P75/i688

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R&D Technical Report P75/i688

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Aztec West, Almondsbury
Bristol BS12 4UD

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1 85705 240 4

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This document was produced under R&D Project P75/i688 by:

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WRc Report No.: EA 4305

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FOREWORD

This report, which reviews petroleum products produced from the refining of crude oil in order to identify priorities for pollution control, is one of a series of five produced under the Environment Agency/SNIFFER Phase IV EQS contract.

The other reports prioritise the following generic groups of compounds; PCBs, polycyclic aromatic hydrocarbons (PAH), tracers and corrosion inhibitors.

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EXECUTIVE SUMMARY

Petroleum products are derived from crude oil and are very complex mixtures of organic chemicals which vary widely in molecular weight, physico-chemical properties, environmental fate, behaviour and toxicity. On the basis of annual production/consumption figures the most important products to man are (in this order); automotive gasoline (“petrol”), automotive diesel fuel, residual fuel oils (Nos 4, 5 and 6) and jet fuel (kerosine). Despite much lower production volumes, lubricating oils (particularly engine oils) are also very important. Of lower importance are fuel oils for domestic heating purposes (i.e. Nos 1 and 2). The increasing production volumes are broadly reflected in an increased risk of entry to aquatic ecosystems as indicated by use, storage and transport patterns.

The fate of petroleum products in the aquatic environment is essentially “weathering” by initial abiotic processes, followed by subsequent biodegradation and accumulation of residual hydrocarbons in the sediments. Petroleum products are comprised of a great many hydrocarbons, all with different physico-chemical properties. These properties along with environmental parameters such as wind speed, temperature, sunlight and mixing action lead to rapid changes in the relative hydrocarbon composition of a spilled product, such that it does not resemble the parent product for long. This mechanism of change is known as “weathering” of which volatilisation and dissolution are the key processes. Low molecular weight compounds are normally completely volatilised from surface spills of petroleum products in just a few days, although as the carbon range of a product increases, the fraction of volatile, water soluble hydrocarbons decreases, so that after a spill an increasingly greater proportion remains as a slick on the surface of the water body.

Following the initial removal of the lighter hydrocarbons through volatilisation and dissolution, the heavier less volatile/soluble compounds either adsorb to suspended solids and subsequently settle in the sediments or, for the residual fuel and lubricating oils in particular, assume a tar like consistency and sink where the residual sticks to suspended solids, sediments and other exposed substrates (e.g. biota). Biodegradation is the primary removal process of the residual and is limited in natural ecosystems by the low water solubility, high molecular size and viscosity of these compounds. Depending on extent of microbial adaptation, dissolved oxygen concentrations, temperature, pH and nutrient status, biodegradation of the hydrocarbons remaining after initial “weathering” of gasolines, kerosine, other distillate fuel oils, residual fuel oils and lubricating oils, generally occurs within the order of weeks, months, months/years, years and years, respectively.

Comparable data indicate that petroleum products produced as a result of atmospheric distillation of crude oil (i.e. all products except lubricating *base* oils) are of moderate to high acute toxicity to aquatic organisms in the laboratory, where concentrations of dissolved hydrocarbons are maintained throughout the test period (effect loads/concentrations = 0.9-32 mg l⁻¹). In contrast, available data reported for lubricating *base* oils indicate that these products are not acutely toxic to aquatic organisms (effect loads/concentrations = >10 000- >100 000 mg l⁻¹), although the inclusion of a wide range of performance-enhancing additives can increase the toxicity of a limited number of these products by up to a thousand-fold. Nevertheless, under field conditions this intrinsic *acute* toxicity of petroleum products is not fully expressed due to rapid removal of the soluble fraction through volatilisation. In the long-

term, adverse effects may be caused by chronic exposure to toxicants such as PAH and/or through physical fouling of organisms by the viscous, post-weathering residual.

Assessing the bioaccumulation potential of petroleum products presents its own difficulties, since each constituent hydrocarbon only accumulates to the extent determined by its own physico-chemical properties. Given the rapid removal of the lighter, water soluble hydrocarbons by volatilisation, bioaccumulation of $<C_{10}$ hydrocarbons is expected to be minimal or non-existent under field conditions, whereas the reduced uptake potential of the large $>C_{30}$ molecules limits the accumulation of these compounds (CONCAWE 1996). Therefore, under most conditions, petroleum products are unlikely to be accumulated in aquatic organisms to high levels. This is supported by the limited number of reported BCFs (8.5, 20, 88 and 159).

Priorities for pollution control have been determined on the basis of potential for significant input to aquatic ecosystems, persistence and potential for long-term effects. As a result, automotive diesel fuel, residual fuel oils (Nos 4-6) and *used* lubricating oils have been identified as HIGH priority for control; automotive gasoline, Fuel Oil No 2 (diesel), *unused* lubricating oils and greases have been defined as MEDIUM priority; jet fuel (kerosine) and white medicinal oils have been assigned to a LOW priority category; while, Fuel Oil No 1 (kerosine), aviation gasoline and kerosine solvents have been identified as NOT a priority for control. The results of the exercise essentially reflect the outcome of combining risk of entry of a product to aquatic environments in significant quantities and potential for long-term effects on ecosystems as a result of chronic toxicity or physical fouling of biota. Automotive diesel fuel followed by residual fuel oils (Nos 4-6) strike the balance between these two parameters most closely and so have been identified as having the highest priority for control.

1. INTRODUCTION

Crude oil is a material of biological origin formed over many millennia as a deposit in rocks under the combined influences of temperature and pressure. The nature of the crude depends upon the original biological source material and the geochemical forces to which it has been subjected (Betton 1994). Due to this variability, and in order to yield a range of performance-based petroleum products, crude oils are subjected to a variety of refining/treatment processes.

The petroleum products derived from crude oil are very complex mixtures of organic chemicals which vary widely in molecular weight, physico-chemical properties, environmental fate, behaviour and toxicity. On the basis of these properties, along with the risk posed by each product to enter aquatic environments in significant quantities, the petroleum products produced by the modern refinery can be prioritised in terms of potential for long-term effects on health of aquatic ecosystems.

The generic product groups reviewed in this report are as follows:

- Gasolines
- Kerosines
- Distillate fuel oils (other than kerosine)
- Residual fuel oils
- Lubricating oils

Section 2 explores further the rationale for selecting these groups for prioritisation, Section 3 summarises production volumes, use patterns and routes of entry to surface waters, while Section 4 gives details of reported concentrations in aquatic environments. Sections 5 and 6 summarise the fate and toxicity of petroleum products and give details relating to the measurement of these parameters for such complex mixtures, while Section 7 prioritises the reviewed products on a use-related basis. Full details pertaining to all these issues are given in the product profiles in Appendices A and B.

2. RATIONALE FOR SELECTION OF PETROLEUM GROUPS FOR REVIEW

2.1 Terminology

Before giving the rationale for selecting the petroleum products reviewed in this report, it is worth explaining the often complex terminology associated with naming different products.

The Environment Agency initially requested a review of “fuel oils”. In the parlance of the American Society for Testing and Materials (ASTM, cited in IARC 1989) these are products (Nos 1, 2, 4, 5 and 6) chiefly used in burners for domestic and industrial heating, for raising steam in electricity generation and for marine propulsion. However, the lighter fuel oils (Nos 1 and 2) also closely approximate kerosine and diesel oil, respectively, in terms of hydrocarbon composition and physico-chemical properties. The latter products are used as jet and automotive fuels. Moreover, the issue is further confused by the fact that diesel fuels are classified in the US as Diesel Fuel Nos, 1, 2 and 4, with No 1 being equivalent to kerosine, No 2 equivalent to the automotive fuel known in Europe simply as “diesel” and No. 4 being a marine fuel oil. These products all derive from the crude oil refinery process. As is discussed in the next section, gasoline (“petrol”) and lubricating oils are the two other generic groups of products derived from this process and so are also reviewed in this report.

To avoid confusion and to enable a better comparison of data, the various petroleum products are reviewed in this report under clearly defined headings, regardless of the use for which they are intended. However, the different uses of the products are identified and discussed (e.g. kerosine both as a heating oil and a jet fuel). The headings are; Gasolines, Kerosines, Distillate Fuel Oils other than Kerosine (i.e. diesel), Residual Fuel Oils and Lubricating Oils. Given their different use pattern and conditions of manufacture, data for the latter are provided separately in Appendix B.

2.2 Crude oil refining and selection of groups for review

The selection of petroleum groups for review is based on the characteristic properties of the different streams produced from crude oil refinery processes. A similar approach has been proposed by the Oil Companies European Organization for Environmental, Health and Protection (CONCAWE 1995). To gain some appreciation for the choice of groups, it is useful to have an outline knowledge of the basic steps to the refining process.

Crude oils are complex mixtures of a vast number of individual chemical compounds. Each oil is a unique mixture, not matched exactly in composition or properties by any other sample of crude oil. The bulk of compounds in crude oil are hydrocarbons including alkanes (e.g. paraffins), cycloalkanes (e.g. naphthenes) and aromatic hydrocarbons (e.g. benzene, benzene derivatives and fused benzene ring compounds). In addition, sulphur compounds make up <0.1-10% of crude oil, with nitrogen and oxygen compounds present at less than 1%. Metallic compounds may be present in the mg l⁻¹ range (e.g. nickel and vanadium) (IARC 1984).

The two key refining steps are atmospheric and vacuum distillation. These processes are illustrated schematically in Figure 2.1.

In atmospheric distillation, the crude oil is heated and fractionally distilled at atmospheric pressure to yield narrower boiling range streams. This process produces petroleum gasses, distillates (e.g. naphtha, kerosine and gas oil) and an atmospheric residue. The distillates are further modified by processes such as cracking, reforming, hydrogenation, etc to produce new petroleum streams that are ultimately treated and blended to produce the broad petroleum groups gasolines, kerosines, light (distillate) fuel oils (i.e. kerosine and diesel) and heavy (residual) fuel oils.

The atmospheric residue may be further fractionated by distillation under vacuum. This yields vacuum distillates and a vacuum residue, both of which may be further processed to give new petroleum streams. In particular, vacuum distillates can be further refined by solvent extraction or hydrogenation which reduces their aromatic hydrocarbon content to ultimately form the mineral base stocks used in lubricating oils.

Figure 2.1 Basic stages of the crude oil refinery process

3. PRODUCTION, USE AND ROUTES OF ENTRY TO THE AQUATIC ENVIRONMENT

3.1 Gasolines and fuel oils

Specific details for each product group are outlined fully in Appendix A.

3.1.1 Gasolines

Commonly known as “petrol” in the UK, gasoline is an extremely important energy source and is the primary product of most petroleum refineries. Gasolines are chiefly used in internal combustion engines to power passenger cars and other types of vehicles including buses, trucks, motorbikes and aircraft, and can broadly be divided into two use categories; automotive gasoline and aviation gasoline (IARC 1989). Annual consumption in Europe (1992) was reported to be over 100 000 thousand (100 million) tonnes (CONCAWE 1992). A corresponding figure of 27 792 thousand tonnes has been reported for UK production in 1992 (Betton 1994), equal to 32.5% of all products produced from crude oil. The main route of entry to the aquatic environment is likely to be as a result of accidental spillage of automotive gasoline during storage and transport. Accidents involving road tankers and ruptured pipelines are a particularly significant source of input to surface waters. In addition, leaks from corroded underground storage tanks can cause widespread gasoline contamination of groundwaters and, potentially, surface waters.

3.1.2 Kerosines

The most important use of kerosines is in the blending of aviation fuels, although they are also used as domestic and industrial heating fuels. In the US, kerosine-based heating oils are marketed as Fuel Oil No 1 (IARC 1989). Kerosines also find some use as solvents in a wide range of products (e.g. cleaning formulations, insecticides, anti-foams and mould release agents). Kerosines may contain performance-enhancing additives that are specific for an intended use, but they are otherwise virtually indistinguishable on the basis of their gross physico-chemical properties. Annual European figures (1985) of 24 376 and 22 787 thousand tonnes have been reported for jet fuel production and consumption, respectively (cited in IARC 1989). A corresponding figure of 9618 thousand tonnes has been reported for UK production in 1992 (Betton 1994), equal to 11.5% of all products produced from crude oil. The main route of kerosine entry to the aquatic environment is likely to be as a result of accidental spillage of aviation fuel and heating oil during storage, transport and use.

3.1.3 Distillate (light) fuel oils other than kerosine

Distillate fuel oils consist of distilled process streams and are defined by The American Society for Testing and Materials (ASTM) as Fuel Oil Nos 1 and 2. In general, “distillate fuel oils” are used as burner fuel for domestic and industrial heating and for raising steam in the generation of electricity. However, the basic physico-chemical properties of Fuel Oil Nos 1

and 2 as used for heating purposes, are very similar to the kerosine and diesel fuels used in aviation and road transport, respectively. The final products are treated as required for a particular application and may contain additives that are specific for the intended use, but they are otherwise virtually indistinguishable (IARC 1989). Fuel Oil No 1 is therefore considered separately in the section on kerosines (3.1.2).

Fuel Oil No 2 (diesel) is used in most home heating installations and in many medium capacity commercial or industrial burners (IARC 1996). Moreover, Fuel Oil No 2 is used far more widely for heating purposes than Fuel Oil No 1 (kerosine), although the use of both products for heating has declined, with transportation finding the greatest use. Automotive diesel fuel is chiefly used in heavy transportation services such as trains, trucks, buses and river boats. It is also finding increasing use in private vehicles.

Production figures specifically relating to Fuel Oil No 2 are not available, although a figure of 26 057 thousand tonnes has been reported for UK automotive diesel production in 1992 (Betton 1994), equal to 30.5% of all products produced from crude oil. The main route of entry to the aquatic environment of these products is likely to be as a result of accidental spillages during storage, transport and use, particularly road run-off of automotive diesel fuels and direct input to surface waters from motor boats.

3.1.4 Residual (heavy) fuel oils

Residual fuel oils are derived from residues remaining after the processes used to produce distillate fuel oils (see Section 3.1.3). The American Society for Testing and Materials (ASTM) define residual products as Fuel Oil Nos 4, 5 and 6 (IARC 1989). Fuel Oil Nos 5 and 6 are also known as Navy Fuel Oil and Bunker C Fuel Oil, respectively, while Fuel Oil No 4 is essentially equivalent to Diesel Fuel No 4 (IARC 1989, OHM/TADS 1985). Fuel Oil Nos 5 and 6 are heavy, residual products. However, while Fuel Oil No 4 is usually a “light” residual, it sometimes is, or contains, a heavy distillate and so is often referred to as “distillate marine fuel oil” (IARC 1989).

In general, residual fuel oils are used by electric utilities, the maritime industry, industrial and commercial plants, and in the petroleum industry for the production of process steam, space and water heating. Electric power generation is the most important use, with 39% of total US domestic consumption used for this purpose in 1983 (IARC 1989). Production/consumption figures specifically relating to each residual product are not available, although IARC (1989) have reported respective values of 233 256 and 103 862 thousand tonnes for total residual oil produced in the 24 countries of the OECD (1985 figures). This contrasts with corresponding production/consumption figures of 418 508 / 199 351 and 444 033 / 228 964 thousand tonnes in 1980 and 1975, respectively. The figures suggest a general decrease in the manufacture and use of these products. A corresponding figure of 13 204 thousand tonnes has been reported for UK production in 1992 (Betton 1994), equal to 15.5% of all products produced from crude oil. The main route of residual fuel oil entry to the aquatic environment is likely to be as a result of accidental spillage of distillate marine fuel and heating oil during storage, transport and use.

3.2 Lubricating oils

Specific details are outlined fully in Appendix B.

Lubricating oils are substances intended to reduce friction between surfaces in relative motion. They may also serve other, secondary purposes, such as liquids for heat transfer, metal processing, corrosion protection and medicinal/food uses. “Lubricant *base* oils” are vacuum distillates of a crude oil refinery which have undergone some finishing process to produce a specific *base* oil, whereas a “lubricating oil” is considered to be a commercial end product, which may or may not contain performance enhancing additives.

The principal base oils are used in a range of products for lubrication of internal combustion engines and a wide variety of industrial, non-engine machinery such as gears, bearings and pumps. Total world production and consumption figures in 1980 for lubricant base oils was reported to be 26 100 and 23 800 thousand tonnes, respectively (Stewart and Helm 1980, cited in IARC 1984). Corresponding figures for Western Europe were 6500 and 6000 thousand tonnes. In addition, a figure of 973 thousand tonnes has been reported for UK production in 1992 (Betton 1994), equal to 1% of all products produced from crude oil. In 1981, over 50% of all lubricating oils sold were for use as automotive and engine oils (Wills 1980, cited in IARC 1984). The main route of entry for large quantities of lubricating oils to the aquatic environment is likely to be as a result of accidental/intentional spillage during storage, transport and use. Some examples include, road run-off of engine oils (used crank case oil is the main source of petroleum hydrocarbons, particularly PAHs, in road run-off; Maltby *et al* 1995), unlawful disposal of used engine oils directly into surface waters and surface water drains, discharge of used/unused oils from river boats and barges and release of lubricating oils from machinery (e.g. gears and pumps) that comes into close contact with surface waters (e.g. abstraction points, weirs, locks, etc).

4. REPORTED CONCENTRATIONS OF PETROLEUM PRODUCTS IN AQUATIC ENVIRONMENTS

As discussed in Section 5, differences in the physico-chemical properties of individual hydrocarbon constituents of petroleum products (i.e. solubility, vapour pressure, etc), along with various “weathering” processes, lead to very rapid changes in relative hydrocarbon composition following a spill. This makes it very difficult to associate the presence of individual compounds with a particular parent product. In other words, once spilt into surface waters, individual hydrocarbons may be identified but there is often no way to link their presence to a particular source or product, particularly since these compounds occur in numerous substances, some of natural origin. It is probably for this reason that few environmental concentrations of whole petroleum product have been reported, even in terms of total soluble hydrocarbons (D. Short, CONCAWE, Pers. Comm., 1996).

4.1 Published data

The limited published data include aviation kerosine and residual fuel oil concentrations of 0.5-1 and 0.01-0.02 mg l⁻¹ in a small stream and the Gulf of Bothnia, following a pipeline rupture and a tanker grounding, respectively (Guiney *et al* 1987 and Vainio *et al* 1987). These concentrations relate to total hydrocarbons associated with each spilt product. In addition, respective soluble and total concentrations of 20-46 and 37-56 mg l⁻¹ of hydraulic oil have been detected in samples of industrial cooling water (Nicholson and Taylor 1975, cited in IARC 1984).

These appear to be the only published data relating to *whole* petroleum products measured in surface waters. However, Maltby *et al* (1995) have reported total hydrocarbon concentrations of 1014-1806 mg kg⁻¹ in sediments of small northern England streams receiving motor-way run-off chiefly consisting of used crank case oil. These values are expressed in terms of lubricant *base* oil-equivalents.

A limited amount of data relating to spillage quantities of different products have also been reported (see Appendices A and B), although these isolated incidents provide little indication of the potential for different petroleum products to enter surface waters.

4.2 Data supplied by the Scottish Environment Protection Agency

4.2.1 Consented discharges

Consented discharges in SEPA East and West Region for various refineries, depots, dockyards and chemical manufacturers range from 5 to 90 mg l⁻¹, expressed as “total” oil concentration as measured either by infrared or gravimetric analysis (calibrant unknown). The consents do not identify individual hydrocarbon concentrations arising from specific petroleum products (I. Ridgeway, Pers. comm. 1996).

4.2.2 Pollution incidents

Data provided by SEPA East Region (1994-1996) indicate that spills of a variety of petroleum products (e.g. kerosine, automotive diesel, heavy fuel oil, etc) is not uncommon in this region. The spills generally originated from storage tanks and pipelines at a variety of sites. In all cases no fish kills were observed, although pollution of receiving surface water was often “significant”. Actual dissolved hydrocarbon or “total oil” concentrations were not recorded (I. Ridgeway, Pers. comm. 1996).

5. FATE, BEHAVIOUR AND PERSISTENCE OF PETROLEUM PRODUCTS IN THE AQUATIC ENVIRONMENT

The fate of petroleum products in the aquatic environment is essentially “weathering” by initial abiotic processes such as photolysis, volatilisation, dispersion and dissolution, followed by subsequent biodegradation and accumulation of residual hydrocarbons in the sediments (Bongiovanni *et al* 1989). Each of these processes, along with available rate data for each petroleum product, is discussed in turn.

5.1 Initial abiotic fate of spilled petroleum products (“Weathering”)

Petroleum products are comprised of a great many hydrocarbons, all with different physico-chemical properties (e.g. vapour pressure and solubility). These properties along with differing environmental parameters such as wind speed, temperature, sunlight and mixing action leads to rapid changes in the relative hydrocarbon composition of a spilled product, such that it does not resemble the parent product for long. This mechanism of change is known as “weathering” and consists of five “key” processes. These are; photolysis, “mousse” formation, dispersion, volatilisation and dissolution (Mackay 1987). These processes are highly interactive (see Figure 5.1), although volatilisation and dissolution are perhaps the most important as they exert the greatest impact on the relative hydrocarbon composition of a spilled petroleum product in water.

Figure 5.1 The five key processes determining the short-term fate of spilt petroleum products (Mackay 1987)

5.1.1 Photolysis

Photolysis may affect the behaviour of a spilled product through the absorption of photolytic energy to form oxygenated active chemical species (e.g. peroxides, hydroperoxides, phenols, alcohols and quinones). These species are generally more soluble than the parent hydrocarbon, have greater surfactant properties and may be of greater toxicity. The increased surfactant properties can lead to increased “mousse” formation and oil-in-water dispersion (Mackay 1987).

There are no available photolysis data relating to removal of specific hydrocarbons from surface slicks of the petroleum products outlined in this review.

5.1.2 “Mousse” formation

Emulsification may occasionally result in the formation of stable “water-in-oil” emulsions known as “chocolate mousse”, which float on the water surface and eventually drift to shoreline or river banks, sometimes as tar balls (Foght and Westlake 1987, Mackay 1987). However, high mixing energy is required to cause this emulsion and, with the exception of large freshwater bodies or swiftly moving rivers, sufficient mechanical energy will not usually be available for mousse formation (Foght and Westlake 1987).

There are no available data relating to mousse formation following spills of the petroleum products outlined in this review.

5.1.3 Dispersion

The strong currents and areas of “white water” in moderate to fast flowing rivers can lead to significant “oil-in-water” dispersion. Dispersion of oil from the surface slick into the water column is very important, since the increased area of the dispersed droplets facilitates dissolution of soluble hydrocarbons (Mackay 1987, Foght and Westlake 1987). As discussed in Section 6, it is the dissolved fraction of dispersed hydrocarbons that exert a direct toxic effect on exposed aquatic organisms in the short term, although the dispersed oil remaining as undissolved droplets still has the potential to cause harmful effects through physical fouling of organisms.

5.1.4 Volatilisation and dissolution

These processes are similar in that they both consist of diffusive transfer of hydrocarbons from the oil phase into a receiving phase (i.e. air or water). Hydrocarbons differ greatly in their tendency to migrate into these phases as indicated by vapour pressure in the case of air and aqueous solubility in the case of water. In both cases, the preferential transfer of selected compounds from the slick results in a profound change in hydrocarbon composition and in altered rates of transfer. For example, as volatilisation progresses its rate falls and the parent product becomes less volatile due to preferential depletion of the more volatile compounds. Similarly, as dissolution progresses a petroleum product becomes less soluble (Mackay 1987).

Rate of volatilisation

Depending on environmental conditions, low molecular weight compounds are completely volatilised from surface spills of petroleum products in just a few days (Foght and Westlake 1987). Indeed, gasolines, which consist chiefly of compounds in the C₄-C₁₂ range, are up to 80% volatilised within 6 hours following a spill to surface water, with >95% of the monoaromatic constituents (e.g. benzene, toluene, ethylbenzene and xylene) which make up 87-95% of the water soluble fraction, being removed within 24 hours (CONCAWE 1992).

These “light” compounds will also be volatilised rapidly from surface spills of heavier petroleum products such as kerosine, other distillate fuel oils (e.g. Fuel Oil No 2, automotive diesel) and residual fuel oils (Fuel Oils Nos 4 to 6). However, as the carbon range for each of these product groups increases (C₉-C₁₆, C₁₁-C₂₀ and up to C₅₀, respectively), the fraction of volatile, water soluble hydrocarbons decreases, so that after a spill to surface water an increasingly greater amount remains as a slick on the surface followed by subsequent sinking and accumulation in sediments. This is particularly true of residual fuel and lubricating oils. The ultimate fate of a product residue remaining in a water body after initial weathering processes, is discussed in the following section.

5.2 Ultimate fate of residual petroleum hydrocarbons

5.2.1 Adsorption and sedimentation

Following the initial removal of the lighter hydrocarbons from a surface water slick through volatilisation and dissolution, the heavier less volatile/soluble compounds will either adsorb to suspended solids and subsequently settle in the sediments or, for the residual fuel and lubricating oils in particular, assume a tar like consistency and sink where the residual will stick to suspended solids, sediments and other exposed substrates (e.g. biota). The loss of the small fraction of lighter hydrocarbons from these products only speeds up the sinking process by increasing the density of the remaining product. The lightest distillate fuel oil, kerosine (Fuel No 1) is unlikely to exhibit this phenomenon, although the residual remaining after weathering will float for some time, with some adsorption of hydrocarbons to suspended solids and sediments (CONCAWE, Pers. Comm. 1996).

For the heavier hydrocarbons remaining after weathering, biodegradation is likely to be the primary removal process and is probably rate limited in natural ecosystems by the low water solubility and molecular size of these compounds. In addition, biodegradation may also play a part in the removal of the small fraction of non-volatilised water soluble hydrocarbons. This process is discussed in the following section.

5.2.2 Biodegradation

Microbial utilisation of hydrocarbons as a sole energy source is highly dependent on the viscosity of the product, the hydrocarbon compounds in the petroleum mixture, the degree of microbial adaptation and on environmental conditions (particularly oxygen availability) (Xie *et al.* 1995). Each of these issues is discussed in turn, although each spill of a petroleum

product is unique and observations concerning biodegradability of different products can only be limited to generalisations (Foght and Westlake 1987).

Viscosity of the product and molecular structure of hydrocarbon constituents

In general, products with a higher content of larger alkanes (i.e. >C₃₀), cycloalkanes and branched/substituted alkanes are more resistant to biodegradation than products consisting of much “lighter” molecules. Hence, residual hydrocarbons following a spill of gasoline to surface water (if any) will be biodegraded more rapidly than the hydrocarbon constituents of residual fuel and lubricating oils, especially since the former will dissolve in the aqueous phase.

The surface area exposed to microbial attack is of importance in determining biodegradation potential of a spilled petroleum product. Heavier viscous products such as residual and lubricating oils present a smaller surface area for attack and so are more resistant to biodegradation. Similarly tar balls and “mousse” emulsions have a limited surface area which restricts the diffusion of oxygen and nutrients to the interior and therefore decreases biodegradation (Foght and Westlake 1987).

Microbial adaptation

Micro-organisms with the ability to utilise hydrocarbons as an energy source are ubiquitous, although they are often present in such low numbers that there may be a substantial lag period before biodegradation is observed (CONCAWE 1992). Aquatic environments recently or historically exposed to hydrocarbons have a higher percentage of micro-organisms adapted to these compounds than “pristine” areas. Generally, in unpolluted systems hydrocarbon degraders constitute less than 0.1% of the total heterotrophic population, whereas in oil-polluted systems the incidence of micro-organisms capable of degrading hydrocarbons may increase to 100% of the population (Foght and Westlake 1987).

Influence of environmental parameters (e.g. oxygen availability)

Perhaps the most important environmental requirement for rapid biodegradation is availability of oxygen. Oxygen is required for extensive hydrocarbon biodegradation, with anaerobic removal being very slow or non-existent (Foght and Westlake 1987). This causes a particular problem for the large hydrocarbon molecules of distillate fuel, residual fuel and lubricating oils, which ultimately become adsorbed to sediments. The general lack of oxygen in bottom sediments and hence biodegradation, may lead to the persistence of these compounds for many years.

Other environmental parameters that can affect the rate of biodegradation include temperature, pH and nutrient status (Foght and Westlake 1987).

Summary of reported data

Standard tests for biodegradability were originally developed only for water soluble materials. However, “ready” biodegradability tests (i.e. complete breakdown to CO₂) have become widely accepted as suitable for providing a first indication of whether a complex petroleum product will biodegrade in aerobic environments (CONCAWE 1992). Examples include the modified Sturm test and the OECD closed bottle test (301A). However, these tests are not used consistently to assess biodegradation potential of petroleum products in the aquatic environment. A test for “inherent” biodegradability (i.e. only primary breakdown of a parent product to its metabolites) is often used (e.g. CEC-L-33-A-93, first developed for testing outboard motor lubricating oils). Moreover, as with toxicity testing (see Section 6), biodegradation studies may be carried out on just the water-soluble fraction of the test material or on the whole petroleum product. When assessing the intrinsic environmental hazard posed by biodegradation of a product, it may be appropriate to test only the water soluble fraction. However, to determine the actual persistence of a product, it is necessary to test the whole petroleum mixture (CONCAWE 1992).

The inconsistencies in the methodologies used to obtain the figures reported in Appendix A, makes comparison of the limited rate data available very difficult. Nevertheless, periods for biodegradation of the hydrocarbons remaining after initial “weathering” of petroleum products are summarised below:

PRODUCT	APPROXIMATE PERIOD FOR BIODEGRADATION OF RESIDUAL PRODUCT
Gasolines	Weeks
Kerosine	Months
Other Distillate Fuel Oils (No 2, automotive diesel)	Months/Years
Residual Fuel Oils (Nos 4 to 6)	Years
Lubricating Oils	Years

6. TOXICITY AND BIOACCUMULATION OF PETROLEUM PRODUCTS IN AQUATIC ORGANISMS

6.1 Assessing aquatic toxicity and bioaccumulation of complex oil mixtures in laboratory tests

6.1.1 Assessment of aquatic toxicity

Before summarising the toxicity of various petroleum products, it is worth outlining a few complications that can arise in the testing of these complex mixtures in the laboratory.

The majority of internationally recognised guidelines for toxicity testing are usually concerned with assessing the toxicity of single compounds. However, such methods are inappropriate for testing the toxicity of oils, which are very complex mixtures of hydrocarbons with widely varying solubilities. It is essential for valid testing that all the constituents of a petroleum product are fully represented in an aquatic test medium in keeping with their respective water solubilities (Bennet *et al* 1990). In other words, to accurately assess the “intrinsic” toxicity of a petroleum product, test organisms should be exposed to the whole range of compounds that are water soluble to one extent or another, since it is only this fraction which is bioavailable. In addition, given the complexity of relating individual hydrocarbons in the aqueous phase to a specific parent product, effects observed in test organisms exposed to a soluble fraction, must be related in some way to the actual quantity of the petroleum product added to the test medium. CONCAWE have proposed a method for assessing the intrinsic toxicity of “whole” petroleum products to overcome these problems (CONCAWE 1992, 1995). The method makes use of the “Water Accommodated Fraction” (WAF) as described below.

Water Accommodated Fractions (WAFs)

Methodology

WAFs are prepared by mixing a known quantity of a petroleum product with a known volume of test medium (the “loading rate”). A WAF is an aqueous medium containing only that fraction of a product which remains in the aqueous phase once the source of mixing energy has been removed and after a period sufficient for phase separation (usually 24 hours). The product may be present either in true solution or as a stable dispersion/emulsion. If the dispersed material is removed by centrifugation or filtration, the medium is sometimes referred to as the Water Soluble Fraction (WSF). However, the use of WAFs is preferred to represent media which may contain a fraction of the oil product in an emulsified or dispersed form along with the fraction in true solution (CONCAWE 1992). At any particular loading rate, the resulting aqueous concentration of each chemical constituent of a petroleum product is a function of the relative volumes of the water and oil phases, the partition coefficient between the phases and maximum solubility in water.

A series of test media containing varying amounts of a product can be prepared in one of two ways:

- preparation of a single WAF at a high loading rate which is then used to produce a dilution series
- preparation of a range of exposure WAFs by preparing individual loading rates for each WAF

The difference between the two approaches can be illustrated with a hypothetical example, in which a petroleum product is to be tested at a range of concentrations corresponding to loading rates of 1 to 1000 mg l⁻¹. If WAFs are prepared individually at each loading rate, the least water soluble components may reach their maximum concentrations in the WAF prepared at the lowest loading rate and their concentration will not change as the loading rate is increased. Components with progressively higher solubilities will reach saturation at progressively higher loading rates. Thus the composition of the soluble hydrocarbon fraction in the medium will change both quantitatively and qualitatively as the loading rate increases.

In contrast, if a single WAF is prepared at a high loading rate and then diluted, each member of the dilution series will contain dissolved components in the same relative concentrations. Thus, dilution of a WAF prepared at 1000 mg l⁻¹ by factors of 10, 100 and 1000, will produce a series of media containing each component at concentrations 1/10th, 1/100th and 1/1000th of those present in the original WAF. However, at the lowest dilution the concentration of those compounds of lowest solubility may be under-represented. In other words lower than if a corresponding WAF was prepared at a loading rate of 1 mg l⁻¹.

Thus it can be seen that dilution of a single WAF prepared at a high loading rate generates individual exposure concentrations which contain less of the poorly water soluble components, than WAFs prepared individually at each required loading rate. Therefore, WAFs should ideally be prepared at each required ratio of product to water, because a dilution series prepared from a single WAF may lead to an underestimation of the toxicity of a “whole” petroleum product.

Reporting the results from WAF tests

For complex mixtures of poorly water soluble compounds it is misleading to express aquatic toxicity in terms of the measured amount of individual constituents in the aqueous phase (i.e. mg l⁻¹ WSF). This is because, as discussed above, the relative composition of a mixture of compounds changes with different loading rates. Moreover, analysis of the WSF is costly and difficult. A measure such as “Dissolved Organic Carbon” is of limited value, since while it may give an idea of exposure to total number of compounds in the aqueous phase, it does not identify whether the materials measured are toxicants or metabolites (Betton 1994). Therefore, CONCAWE (1992) have proposed that, in order to provide a toxicity value for an oil product that is comparable with an LC/EC50 for a single chemical substance, the result should be expressed in terms of the loading rate. i.e. as the quantity of the “whole” test product added to the aqueous medium.

This point can be illustrated with the following example. Adema (1985, cited in CONCAWE 1992) investigated the toxicity of white spirit to the saltwater crustacean, *Chaetogammarus marinus*. The 96 hour LL50 based on loading rate was 3.5 mg l⁻¹, while the LC50 based on measured concentrations of the dissolved constituents (WSF) was 0.54 mg l⁻¹. Which figure best defines the toxicity of the “whole” oil product? If the objective is to compare the toxicity of white spirit with other chemical and oil products, the loading rate is the most meaningful figure because it allows comparisons to be made on the basis of the amount of product that is required to produce an effect.

The loading rate required to give a particular effect (e.g. 50% mortality) can be expressed in a manner analogous to that used for water soluble products. Thus:

- LL50 value = medial lethal loading rate (analogous to LC50);
- EL50 value = median effect loading rate (analogous to EC50);
- NOEL/LOEL values = No-Observed/Lowest-Observed Effect Loading rate (analogous to NOEC/LOEC).

A major benefit in expressing results in terms of loading rates is that data are of real value when assessing the potential environmental hazard of a petroleum product. Results expressed simply in terms of the measured concentration of the fraction of a product in solution, are of little value, since it is very difficult to extrapolate to a field situation in which the only relevant measures of concentration are the amount of product spilled and the volume of the receiving water. In other words, the loading rate (Girling *et al* 1992).

Toxicity testing of dispersions/emulsions

A dispersion consists of a quantity of a petroleum product distributed uniformly in, but not wholly dissolved in, an aqueous medium (CONCAWE 1992). Data generated by these tests are usually reported in terms of amount of oil added to the water rather than hydrocarbon concentrations actually present in the aqueous phase. Unless the test product has a natural tendency to emulsify, dispersions require either an input of energy (e.g. propeller) or the use of a chemical dispersing agent to maintain the distribution of the product in the test medium. These two requirements place limitations on the testing methods which can be employed. For instance, the constant input of mixing energy may preclude the use of small fragile test organisms such as *Daphnia*, while the use of dispersants may not reflect exposure likely to occur under environmental conditions and could also confuse the toxicity data obtained in the study.

Despite these short-comings, the use of dispersions may provide a more realistic assessment of effects which might result from the introduction of a petroleum product into an aquatic environment (Betton 1994). Such effects include both direct toxicity as a result of exposure to water soluble hydrocarbons and physical fouling of exposed organisms and habitats by dispersed oil droplets. Nevertheless, for determining the intrinsic toxicity of petroleum products, the WAF method is more appropriate than dispersion-type tests. Consequently, the use of WAFs is the preferred method for generating data for regulatory purposes, as the

approach allows for a comparison of the intrinsic toxicity of different petroleum products, as well as a comparison with toxicity data for single water-soluble chemicals (Betton 1994).

6.1.2 Assessing bioaccumulation potential

Study of the bioaccumulation potential of petroleum products also presents some difficulties. Each constituent compound bioaccumulates only to the extent determined by its own physico-chemical properties and so each component needs to be measured independently (CONCAWE 1992). The analytical problems that this presents are aggravated by the similarity of many of these constituents to compounds naturally present in fish. Many oil hydrocarbons in fact enter the metabolic pathways of fish, leading to energy production or incorporation into biomass. Such compounds do not therefore accumulate to the degree that might be predicted on the basis of their partitioning characteristics (Betton 1994).

6.2 Toxicity and bioaccumulation of different petroleum products

Full details for each petroleum group are given in Appendices A and B.

6.2.1 Aquatic toxicity

Intrinsic toxicity

Laboratory tests measuring intrinsic toxicity of petroleum products usually aim to maintain concentrations of soluble hydrocarbons at a maximum level and to avoid losses due to evaporation, abiotic/biotic degradation, etc. This is particularly important since the compounds most responsible for causing acute toxicity are the lighter more soluble hydrocarbons (<C₁₀) (CONCAWE 1996). However, under field conditions this intrinsic toxicity is not fully expressed due to rapid removal of the soluble fraction through volatilisation (i.e. “weathering”, see Section 5.1.4). Nevertheless, in order to rank different petroleum products in terms of relative toxicity and hence identify priorities for control, it is necessary to utilise data obtained in consistent (as far as possible) laboratory studies, in which exposure concentrations of soluble hydrocarbons were maintained.

In light of the above, data obtained in closed WAF tests have been reported in Appendices A and B in preference to other methods. However, where WAF data are limited, the most reliable WSF and oil-in-water dispersion (OWD) values have been reported. This may cause some difficulties in interpretation, since each mixing method represents a very different exposure regime. Any observed differences in toxicity between different tests may be a function not only of specific characteristics of the test material (i.e. solubility of component hydrocarbons, intrinsic toxicity, etc), but also of the different exposure regimes (Linnet *et al* 1996). Nevertheless, acute effect loads/concentrations (IL(C)50, EL(C)50, LL(C)50) for the generic products under review fall within the following ranges (see Appendices A and B):

PRODUCT	ACUTE EFFECT LOAD/CONCENTRATION (mg l ⁻¹)
Gasolines	3.6-18 (WAF)
Kerosine	1.4-25 (WAF)
other Distillate Fuel Oils (No 2, automotive diesel)	2.6-32 (WAF)
Residual Fuel Oils (Nos 4 to 6)	0.9-3.1 (WSF)
Lubricating <i>base</i> Oils	>10 000->100 000 (WAF/WSF)

These data indicate that petroleum products produced as a result of atmospheric distillation of crude oil (i.e. all products except lubricating *base* oils) are of moderate to high acute toxicity to aquatic organisms in the laboratory, where concentrations of dissolved hydrocarbons are generally maintained throughout the test period. In contrast, available data reported for lubricating *base* oils indicate that these products are not acutely toxic to aquatic organisms. However, it should be noted that the inclusion of a wide range of performance-enhancing additives in commercial lubricating oils can increase the toxicity of a limited number of these products. For instance, in toxicity studies conducted on 11 commercial formulations, eight products were not acutely toxic (L(E)L50s >10 000 mg l⁻¹), while the remaining three were of moderate acute toxicity to sensitive aquatic organisms (<10-100 mg l⁻¹) (Girling *et al* 1993) (see Appendix B).

As well as the uncertainties associated with comparing toxicity data from studies which utilised varying methodologies, complications can also arise as a result of variations in toxicity of similar products within a group, due to differences in product composition. For instance, the toxicity of residual fuel oils (Nos 4 to 6) is dependent to some extent on the quantity and type of lower molecular weight blending stocks used in their preparation. Moreover, variations in the relative proportion of performance-enhancing additives can also alter the toxicity of different petroleum products.

Chronic toxicity

Short-term tests may underestimate the chronic toxicity of certain petroleum hydrocarbons as the exposure duration may be insufficient to achieve a toxic threshold within the test organism. However, chronic toxicity data are not generally available for whole petroleum products, although some general predictions concerning long-term effects can be made on the basis of the presence or absence of known chronic toxicants such as polycyclic aromatic hydrocarbons (PAH). In general the heavier distillate/residual fuel oils and certain lubricating oils (particularly used automotive products) contain the highest concentrations of chronically toxic compounds and so have the greatest potential to cause adverse effects following long-term exposure.

Physical fouling of biota, sediments and substrates

The above data chiefly relate to concentrations expressed as WAFs or WSFs which are bioavailable and cause direct acute toxicity as a result of uptake into the organism. However, adverse effects can also be caused through physical fouling of organisms exposed to dispersed droplets and oil-in-water emulsions. Indeed, under field conditions spilled petroleum products of the heavier type (e.g. residual fuel oil, lubricating oils) probably exert their greatest impact through smothering of biota, sediments and other substrates. This can lead to asphyxiation of fish, removal of algae as a food source and the destruction of benthos. The extent of physical fouling can be predicted from the viscosity and fate of petroleum products and does not need to be measured experimentally (CONCAWE 1992).

Indirect effects of high Biochemical Oxygen Demand (BOD)

In addition to the intrinsic toxicity and physical fouling caused by petroleum hydrocarbons, biodegradation of high concentrations of petroleum compounds and dead biota/flora in ecosystems heavily contaminated with oil, can also pose a hazard to aquatic organisms as a result of deoxygenation. However, in the absence of reliable data, this phenomenon has not been pursued.

6.2.2 Bioaccumulation

As discussed in Section 6.1.2, assessing the bioaccumulation potential of petroleum products presents its own difficulties. Each constituent hydrocarbon only bioaccumulates to the extent determined by its own physico-chemical properties and so each compound ideally needs to be measured independently (CONCAWE 1992). Moreover, since many oil hydrocarbons enter the metabolic pathways of fish and are incorporated into the biomass, they are not accumulated to the degree that might be predicted on the basis of their partitioning characteristics (Betton 1994).

Given the rapid removal of the lighter, water soluble hydrocarbons by volatilisation and biodegradation, bioaccumulation of $<C_{10}$ hydrocarbons is expected to be minimal or non-existent under field conditions (CONCAWE 1996). Moreover, the reduced uptake potential of the larger molecules in petroleum products ($>C_{30}$) limits the accumulation of these compounds. Therefore, under most conditions, petroleum hydrocarbons are unlikely to be accumulated in aquatic organisms to high levels. This is true even under laboratory conditions where exposure concentrations in the bioavailable WAF/WSF are maintained. For instance, BCFs of 88-159, 8.5 and 20 have been reported for aquatic organisms following exposure to the WSF of aviation kerosine, an emulsion of Fuel Oil No 2 and Fuel Oil No 6, respectively (see Appendix A).

There are no available laboratory data concerning the inherent bioaccumulation potential of gasolines and lubricating oils, although in the laboratory the former may be accumulated to the highest levels of all (BCFs up to around 200), while the latter is likely to be accumulated to similar or lower levels than the residual fuel oils (i.e. BCFs <20). However, for reasons already discussed, neither group of products is likely to be bioaccumulated to high levels under field conditions, especially in the short term.

7. IDENTIFICATION OF PRIORITIES FOR THE CONTROL OF HAZARDS ARISING FROM PETROLEUM PRODUCTS IN THE AQUATIC ENVIRONMENT

7.1 Background

In assessing the potential risks posed by chemicals in the aquatic environment, a number of issues require consideration. These are: toxicity, bioaccumulation, persistence, exposure concentrations and potential routes of entry. Many schemes of varying complexity are available in the literature which prioritise substances on the basis of these parameters. The scheme proposed in this review adopts the principles of prioritisation schemes devised by WRc for other generic groups of chemicals, which are in turn based on a protocol developed for the DoE for the selection of candidate List I substances that are potentially hazardous to aquatic life (Hedgecote and Cooper 1991).

These schemes generally identify those substances which pose the greatest hazard to the aquatic environment on the basis of their use/production (i.e. scale of potential surface water contamination), toxicity, bioaccumulation and persistence. For each of these parameters, chemicals are classified as either 'HIGH', 'MODERATE' or 'LOW', and a decision tree is followed in order that the substance may be assigned to either 'HIGH', 'MEDIUM', 'LOW' or 'NO' priority categories. However, the complex fate and behaviour of petroleum products in aquatic ecosystems makes necessary some adaptations to the above schemes (e.g. as discussed in Section 7.2.3, acute data reported in the laboratory are not as useful as long-term effects predictions). Furthermore, the scheme adopted in this review is not intended to identify priorities for EQS development, because, as discussed in Sections 5 and 6, complications associated with the fate and toxicity of complex petroleum mixtures, make it impossible to set a single standard that will be protective of organisms exposed to the highly variable hydrocarbon constituents arising from spillages of different parent products to receiving waters. Therefore, the results of the scheme are intended only to identify priorities for pollution control activities.

7.2 Approach adopted for petroleum products

The hazards posed to the health of aquatic ecosystems by the different petroleum products produced by refining crude oil, have been prioritised on the basis of (in this order); 1) potential for significant input to aquatic ecosystems, 2) persistence, and, 3) potential for long-term effects. The rationale for choosing these parameters along with their determination is discussed in the following sections.

7.2.1 Potential for significant input to aquatic ecosystems

The potential for each petroleum product to enter aquatic ecosystems in significant quantities has been assessed semi-quantitatively on the basis of use/transport/storage patterns and

reported UK/European production figures. For instance, the risk of automotive gasoline entering surface waters is considered to be relatively high as a result of road tanker spillages, pipeline ruptures and leaks to groundwater from corroded storage tanks. This high risk coupled with high annual production volumes leads to the classification of gasolines as having a HIGH potential for significant input to aquatic ecosystems. In contrast, although many automotive lubricating oils have a high risk of entry to surface waters through unlawful disposal to drains or road run-off, their annual production is comparatively low. Therefore, in terms of potential for input to significant levels, these products have been assigned to a MEDIUM category. The definitions used in categorising each product according to this parameter are given in Table 7.1.

Reported environmental concentrations of petroleum products have not been used as a parameter in the prioritisation scheme, as very few hydrocarbon concentrations have been measured in natural ecosystems that can be associated with a specific parent product. This is due to the rapid changes that occur to the constituents of a product as a result of weathering processes such as volatilisation and biodegradation (see Section 5). It is therefore not possible to define an “exposure concentration” for the whole product or, consequently, to quantitatively assess the risk of ecotoxicological effects on the basis of laboratory data.

7.2.2 Persistence

The persistence of each petroleum product has been assessed on the basis of *whole* product removal in aquatic ecosystems through both abiotic and biotic means. Note that a reported half-life does *not* equal the time taken for 50% removal of total number of hydrocarbon constituents in a product, but the time taken for 50% removal of the total product mass. In general, this is much shorter for lighter products such as gasoline and kerosine, whose chief constituents are lost very rapidly through volatilisation. Time taken for 100% removal has also been given to indicate the extended persistence of the residual hydrocarbons remaining after initial weathering processes have occurred (see Section 5.1), particularly for the heavier products such as residual fuel oils and lubricating oils. The definitions used in categorising each product according to this parameter are given in Table 7.1.

7.2.3 Potential for long-term effects

Following a spill, aquatic organisms may be either exposed to the water soluble components of a petroleum product and/or to the whole product itself, either in the form of dispersed droplets, emulsion or as the surface slick. In general, any resulting adverse effects will be caused by the intrinsic toxicity (i.e. uptake and bioaccumulation) of the former and/or by physical fouling of biota and substrates by the latter. Despite the availability of acute laboratory WAF/WSF data for comparing the relative intrinsic toxicity of different petroleum products, it is not possible to distinguish between the different products as the data indicate broadly similar acute toxicity.

Table 7.1 Classification categories adopted for prioritisation of petroleum products

Parameter	Category	End-point	Range
Potential for significant input to aquatic ecosystems	HIGH	High risk of entry as implied by use/transport/storage patterns and MODERATE/HIGH production volumes ¹	See Note 1
	MODERATE	Moderate risk of entry as implied by use/transport/storage patterns and MODERATE/HIGH production volumes ¹ ; OR: High risk of entry and LOW production volumes ¹	See Note 1
	LOW	Low risk of entry as implied by use/transport/storage patterns and LOW/MODERATE production volumes ¹	See Note 1
Persistence	LOW	50% removal of total product mass ² 100% removal of total product mass	<1 month <1 year
	MODERATE	50% removal of total product mass ² 100% removal of total product mass	1 month - 1 year 1 year - 5 years
	HIGH	50% removal of total product mass ² 100% removal of total product mass	>1 year >5 years
Potential for long-term effects	HIGH	High levels of known chronic toxicants (e.g. PAH) and/or high potential for physical fouling of biota, sediments and other substrates ³	-
	MODERATE	Moderate levels of known chronic toxicants (e.g. PAH) and/or moderate potential for physical fouling of biota, sediments and other substrates ³	-
	LOW	Low levels of known chronic toxicants (e.g. PAH) and/or low potential for physical fouling of biota, sediments and other substrates ³	-

Notes to Table 7.1

- 1 Production volumes: HIGH = >10 000 (UK)/>100 000 (Europe), MODERATE = 1 000-10 000 (UK)/10 000-100 000 (Europe), LOW = <1 000 (UK)/<10 000 Europe (thousand tonnes per year)
- 2 50% removal does NOT equal time taken for removal of 50% of total number of hydrocarbon constituents in the whole product. In general, this will be much shorter for lighter products such as gasoline and kerosine, whose chief constituents are very volatile hydrocarbons
- 3 Based on viscosity and fate of residual hydrocarbons following initial weathering processes (see Section 5.2)

In any case, acute toxicity is unlikely to be expressed under field conditions due to rapid volatilisation of the light hydrocarbons responsible for toxicity in the short-term. For the lighter hydrocarbon constituents of petroleum products, toxicity increases up to about C₁₀, at which point solubility becomes so low that the hydrocarbons are no longer available for immediate uptake and toxic concentrations are not attained over acute exposure periods (CONCAWE 1996). Therefore, since those compounds responsible for acute toxicity are rapidly removed from the water column under field conditions, chronic toxicity caused by the remaining larger molecules should be used as a parameter for identifying relative hazards posed by different petroleum products to the long-term health of aquatic ecosystems. Since chronic toxicity data are generally not available for whole petroleum products, the level at which known chronic toxicants (e.g. PAH) are present is used as a parameter in assessing the relative potential of different products to cause long-term effects (see the “Description” sections of Appendices A and B). This is supported by potential to cause long-term physical fouling of biota, sediments and other substrates, as identified by the viscosity and fate of residual hydrocarbons following initial weathering processes (see Section 5.2, 6.2.1). The definitions used in categorising each product according to this parameter are given in Table 7.1.

Bioaccumulation of different products has not been used in the prioritisation scheme due to a number of complications, mostly associated with the same weathering and bioavailability issues that affect toxicity of complex hydrocarbon mixtures under field conditions (see above and Sections 5.2, 6.2.2). This is reflected in the very limited, low BCFs reported for petroleum products (8.5, 20, 88, 159), even in laboratory bioassays where hydrocarbon concentrations are generally maintained throughout the exposure period.

7.3 Outcome of the scheme

The scheme outlined in Figure 7.1 has been used to prioritise all the general petroleum product groups that have been reviewed in this report. Products within a group that have distinct uses (e.g. different types of lubricating oils, kerosine used for both aviation and heating purposes, etc) have been prioritised separately, as potential for input based on use patterns and production volumes will have a bearing on the overall categorisation of each product. The numbering broadly identifies further priorities within the categories on the basis of use, storage, transport and production volumes reported for individual products.

The results of the scheme are given fully in Table 7.2 and can be summarised as follows:

HIGH PRIORITY FOR CONTROL

1. Automotive diesel fuel
2. Residual Fuel Oils (Nos 4-6)
3. *Used* automotive engine lubricating oils
4. Other *used* lubricating oils (e.g. 2-stroke, gear transmission, hydraulic, heat transfer, heat treatment, cutting and rolling oils)

MEDIUM PRIORITY FOR CONTROL

5. Automotive gasoline
6. Fuel Oil No 2 (diesel)
7. *Unused* automotive engine lubricating oils
8. Other *unused* lubricating oils (e.g. 2-stroke, gear transmission, hydraulic, heat transfer, heat treatment, cutting and rolling oils)
9. Automotive and industrial greases

LOW PRIORITY FOR CONTROL

10. Jet fuel (kerosine)
11. White medicinal Oils

NOT A PRIORITY FOR CONTROL

12. Fuel Oil No 1 (kerosine)
13. Aviation gasoline
14. Solvents (kerosine)

The results essentially reflect the outcome of combining risk of entry of a product to aquatic environments in significant quantities and potential for long-term effects on ecosystems as a result of chronic toxicity or physical fouling of biota. Automotive diesel fuel followed by residual fuel oils (Nos 4-6) strike the balance between these two parameters most closely and so have been identified as having the highest priority for control. Automotive gasoline has been assigned to a MEDIUM priority category on the basis of its high risk of entry to aquatic ecosystems and its extremely high annual production, despite its lack of long-term effects. In contrast, products with similar physico-chemical and toxicological properties to gasoline (e.g., kerosine based jet fuel and Fuel Oil No 1 for heating) are of LOW or NO priority, due to the minimal risk of entry and low production volumes of these products.

Prioritising the lubricating oils is a less precise exercise as very few data are available in the open literature concerning the toxicity of commercial products which may or may not include performance-enhancing additives. Moreover, chronic toxicity of lubricating oils is also dependent on the relative proportions of *base* oils used in their blending and the severity of refining which the vacuum residuum undergoes to produce the various base oils. Nevertheless, each generic group of lubricating oils as defined by use type, has been prioritised as above. The only exception is for medicinal white oils, which do not lend themselves to the above scheme. Although these products have an inherent potential to cause physical fouling of biota and substrates due their viscous nature, they nonetheless pose such a low risk of entry to aquatic ecosystems and are produced in such small quantities, that their prioritisation category has been adjusted from MEDIUM to LOW. Moreover, these products are refined to such an

extent that they contain no compounds toxic to aquatic organisms following long-term exposure.

There is also strong evidence to suggest that the level of chronic toxicants such as PAH can increase by up to 100-fold in some used lubricating oils (particularly automotive engine oils). This has been accounted for in the prioritisation outlined in Table 7.2.

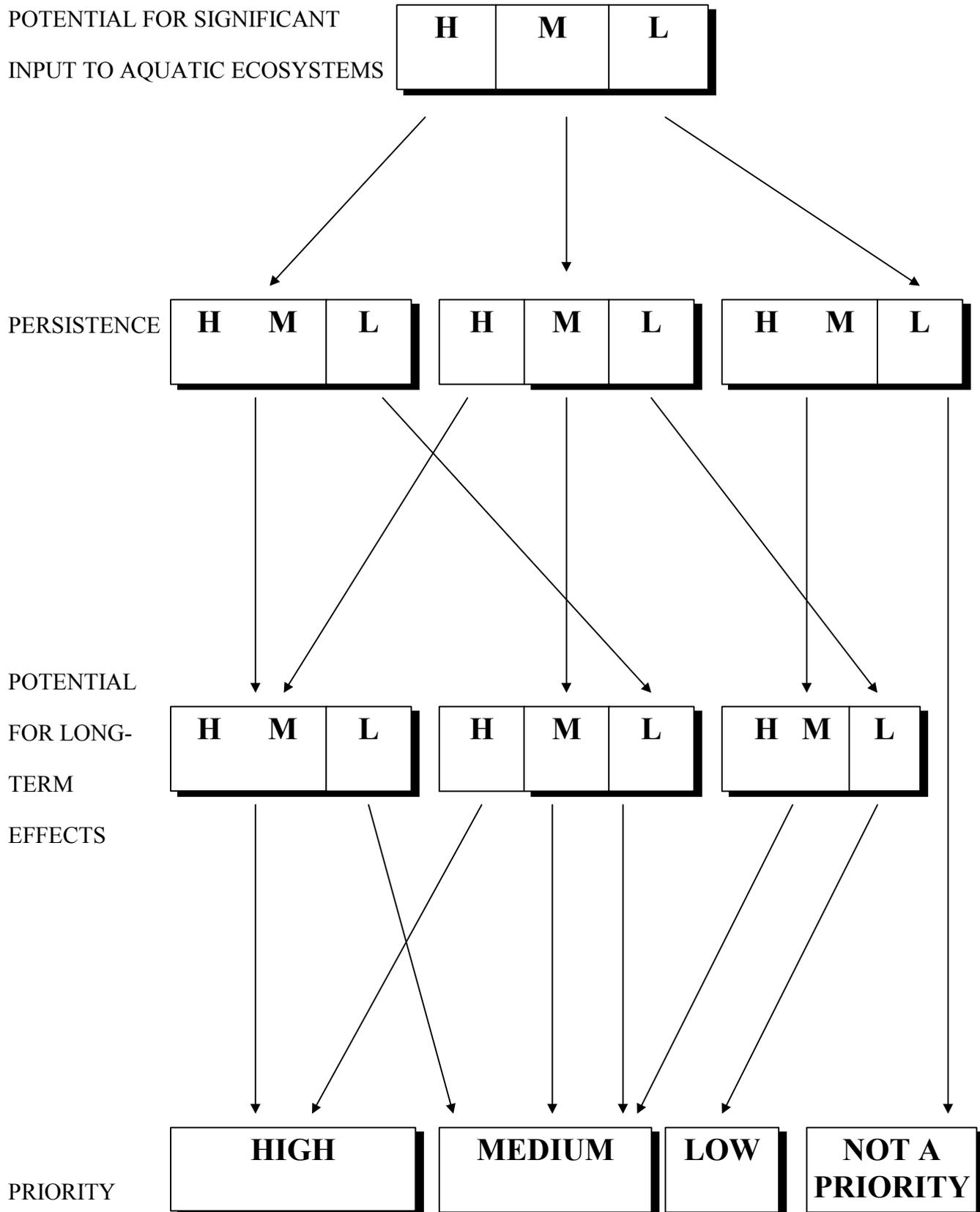


Figure 7.1 Prioritisation scheme based on input, persistence and long-term effects

Table 7.2 Prioritisation of petroleum products on the basis of long-term hazards posed to aquatic environments

Petroleum product	A. Risk of entry to aquatic ecosystems ¹	B. Production volume (thousand tonnes/year)	Potential for sig. input to aquatic ecosystems (A + B)	C. Approx Time for 50%/100% removal of total product mass ²	Persistence (based on C)	D. Potential for chronic toxicity ³	E. Potential for physical fouling of biota and sediments ⁴	Potential for long-term effects (D + E)	PRIORITY
Gasolines									
Automotive gasoline	High	27 792 (UK) ⁵ 100 000 (EUR) ⁶	HIGH	5 hr/3 wk	LOW	Low	Low	LOW	MEDIUM
Aviation gasoline	Low	No data (probably low)	LOW	5 hr/3 wk	LOW	Low	Low	LOW	NOT
Kerosines									
Jet fuel	Moderate	9 618 (UK) ⁵ 24 376 (EUR) ⁷	MODERATE	1 dy/8 mo	LOW	Low	Low	LOW	LOW
Fuel Oil No1	Low	No reliable data (probably low)	LOW	1 dy/8 mo	LOW	Low	Low	LOW	NOT
Solvents	Low	No data (probably low)	LOW	1 dy/8 mo	LOW	Low	Low	LOW	NOT
Distillate Fuel Oils other than kerosine									
Automotive diesel fuel	High	26 057 (UK) ⁵ No data (EUR)	HIGH	6 mo/2 yr	MODERATE	Moderate	Moderate	MODERATE	HIGH
Fuel Oil No 2	Low	No reliable data (probably low)	LOW	6 mo/2 yr	MODERATE	Moderate	Moderate	MODERATE	MEDIUM

Petroleum product	A. Risk of entry to aquatic ecosystems ¹	B. Production volume (thousand tonnes/year)	Potential for sig. input to aquatic ecosystems (A + B)	C. Approx Time for 50%/100% removal of total product mass ²	Persistence (based on C)	D. Potential for chronic toxicity ³	E. Potential for physical fouling of biota and sediments ⁴	Potential for long-term effects (D + E)	PRIORITY
Residual Fuel Oils									
Fuel Oil Nos 4, 5 and 6	Moderate	13 204 (UK) ⁵ 233 256 (EUR) ⁷	MODERATE	2 yr/6 yr	HIGH	High	High	HIGH	HIGH
Lubricating oils									
Engine oils (unused)	Low	973 (UK) ^{5,8} 6 500 (EUR) ^{8,9}	LOW	2 yr/6 yr	HIGH	Moderate	High	HIGH	MEDIUM
Engine oils (used)	High	973 (UK) ^{5,8} 6 500 (EUR) ^{8,9}	MODERATE	2 yr/6 yr	HIGH	High	High	HIGH	HIGH
2-stroke, gear, transmission, hydraulic, heat transfer, heat treatment, cutting and rolling oils (unused)	Low	973 (UK) ^{5,8} 6 500 (EUR) ^{8,9}	LOW	2 yr/6 yr	HIGH	High	High	HIGH	MEDIUM
As above (used)	High	973 (UK) ^{5,8} 6 500 (EUR) ^{8,9}	MODERATE	2 yr/6 yr	HIGH	High	High	HIGH	HIGH
Automotive and industrial greases	Low	973 (UK) ^{5,8} 6 500 (EUR) ^{8,9}	LOW	2 yr/6 yr	HIGH	Moderate	High	HIGH	MEDIUM

Petroleum product	A. Risk of entry to aquatic ecosystems ¹	B. Production volume (thousand tonnes/year)	Potential for sig. input to aquatic ecosystems (A + B)	C. Approx Time for 50%/100% removal of total product mass ²	Persistence (based on C)	D. Potential for chronic toxicity ³	E. Potential for physical fouling of biota and sediments ⁴	Potential for long-term effects (D + E)	PRIORITY
White medicinal oils	Low	973 (UK) ^{5,8} 6 500 (EUR) ^{8,9}	LOW	2 yr/6 yr	HIGH	Low	Low ¹⁰	LOW ¹⁰	LOW ¹⁰

Notes to Table 7.2:

- 1 Based on an assessment of use/transport/storage patterns
- 2 For removal of WHOLE product. i.e. 50% removal does NOT equal time taken for removal of 50% of total number of hydrocarbon constituents in the whole product. In general, this will be much shorter for lighter products such as gasoline and kerosine, whose chief constituents are very volatile hydrocarbons
- 3 Based on level of known chronic toxicants in the product (e.g. PAHs)
- 4 Based on viscosity and fate of residual hydrocarbons following initial weathering processes (see Section 5.2)
- 5 1991 figures
- 6 1992 figure
- 7 1985 figure
- 8 Figure for all lubricating oils, of which around 50% are used as automotive engine oils
- 9 1980 figure
- 10 Although this product has an inherent potential to cause physical fouling of biota and substrates due its viscous nature, it nonetheless poses such a low risk of entry to aquatic ecosystems and is produced in such small quantities (relatively), that its prioritisation category has been adjusted from MEDIUM to LOW

8. CONCLUSIONS

1. Petroleum products derived from crude oil are very complex mixtures of chemicals which vary widely in molecular weight, physico-chemical properties, environmental fate, behaviour and toxicity. On the basis of annual production/consumption figures the most important products to man are (in this order); automotive gasoline (“petrol”), automotive diesel fuel, residual fuel oils (Nos 4-6) and jet fuel (kerosine). Despite much lower production volumes, lubricating oils (particularly engine oils) are also very important. Of lower importance are fuel oils for domestic heating purposes (i.e. Nos 1 and 2). The increasing production volumes are broadly reflected in an increased risk of entry to aquatic ecosystems as indicated by use, storage and transport patterns.
2. The fate of petroleum products in the aquatic environment is essentially “weathering” by initial abiotic processes, followed by subsequent biodegradation and accumulation of residual hydrocarbons in the sediments. Petroleum products are comprised of a great many hydrocarbons, all with different physico-chemical properties. These properties along with parameters such as wind speed, temperature, sunlight and mixing action lead to rapid changes in the relative hydrocarbon composition of a spilled product, such that it does not resemble the parent product for long (hence, there are very few reported environmental concentrations). This mechanism of change is known as “weathering” of which volatilisation and dissolution are the key processes (Mackay 1987). Low molecular weight compounds are completely volatilised from surface spills of petroleum products in just a few days. Indeed, gasolines, which consist chiefly of compounds in the C₄-C₁₂ range, are up to 80% volatilised within 6 hours following a spill to surface water (CONCAWE 1992). These “light” compounds will also be volatilised rapidly from surface spills of heavier petroleum products, although as the carbon range for each of these product groups increases the fraction of volatile, water soluble hydrocarbons decreases, so that after a spill an increasingly greater amount remains as a slick on the surface. This is particularly true of residual fuel oils and lubricating oils.
3. Following the initial removal of the lighter hydrocarbons through volatilisation and dissolution, the heavier less volatile/soluble compounds either adsorb to suspended solids and subsequently settle in the sediments or, for the residual fuel and lubricating oils in particular, assume a tar like consistency and sink where the residual sticks to suspended solids, sediments and other exposed substrates (e.g. biota). Biodegradation is the primary removal process of the residual and is rate limited in natural ecosystems by the low water solubility, high molecular size and viscosity of these compounds. Depending on parameters such as extent of microbial adaptation, dissolved oxygen concentration, temperature, pH and nutrient status, biodegradation of the hydrocarbons remaining after “weathering” of gasolines, kerosine, other distillate fuel oils, residual fuel oils and lubricating oils, generally occurs within the order of weeks, months, months/years, years and years, respectively.
4. Comparable WAF/WSF data indicate that petroleum products produced as a result of atmospheric distillation of crude oil (i.e. all products except lubricating *base* oils) are of moderate to high acute toxicity to aquatic organisms in the laboratory, where concentrations of dissolved hydrocarbons are maintained throughout the test period (effect loads/concentrations = 0.9-32 mg l⁻¹). In contrast, available data reported for

lubricating base oils indicate that these products are not acutely toxic to aquatic organisms (effect loads/concentrations = $>10\ 000$ - $>100\ 000\ \text{mg l}^{-1}$) although, the inclusion of a wide range of performance enhancing additives can increase the toxicity of a limited number of these products by up to a thousand-fold. Nevertheless, under field conditions this intrinsic acute toxicity is not fully expressed due to rapid removal of the soluble fraction through volatilisation. In the long-term, adverse effects may be caused either by exposure to chronic toxicants such as PAH or through physical fouling of organisms by the viscous, post-weathering residual.

5. Assessing the bioaccumulation potential of petroleum products presents its own difficulties, since each constituent hydrocarbon only accumulates to the extent determined by its own physico-chemical properties. Given the rapid removal of the lighter, water soluble hydrocarbons by volatilisation, bioaccumulation of $<C_{10}$ hydrocarbons is expected to be minimal or non-existent under field conditions, whereas the reduced uptake potential of the large $>C_{30}$ molecules limits the accumulation of these compounds (CONCAWE 1996). Therefore, under most conditions, petroleum hydrocarbons are unlikely to be accumulated in aquatic organisms to high levels. This is supported by the limited number of reported BCFs (8.5, 20, 88, 159).
6. On the basis of potential for significant input to aquatic ecosystems, persistence and potential for long-term effects, automotive diesel fuel, residual fuel oils (Nos 4-6) and *used* lubricating oils have been identified as HIGH priority for control; automotive gasoline, Fuel Oil No 2 (diesel), *unused* lubricating oils and greases have been defined as MEDIUM priority; jet fuel (kerosine) and white medicinal oils have been assigned to a LOW priority category; while, Fuel Oil No 1 (kerosine), aviation gasoline and kerosine solvents have been identified as NOT a priority for control. The results of the exercise essentially reflect the outcome of combining risk of entry of a product to aquatic environments in significant quantities and potential for long-term effects on ecosystems as a result of chronic toxicity or physical fouling of biota. Automotive diesel fuel followed by residual fuel oils (Nos 4-6) strike the balance between these two parameters most closely and so have been identified as having the highest priority for control.

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APPENDIX A PROFILES FOR GASOLINES AND FUEL OILS

A1 GASOLINES

Table A1.1 Summary of data for gasoline products

Carbon range	C ₄ -C ₁₂ (1)
Appearance	Clear or amber liquid. Will float in slick on water surfaces (2)
Uses	Automotive and aviation fuel
Boiling point range (°C)	
- Automotive gasoline	22-220 (3)
- Aviation gasoline	25-170 (3)
Flash point (°C)	
- Automotive gasoline	< 40 (3)
- Aviation gasoline	< 40 (3)
Freezing point (°C)	
- Aviation gasoline	< 58 (1)
Density (g cm ⁻³)	
- Automotive gasoline	0.72-0.79 (3)
- Aviation gasoline	0.7-0.75 (3)
Vapour pressure (hPa)	
- Automotive gasoline	350-900 (3)
- Aviation gasoline	360-490 (3)
Octanol-water partition coefficient (log K _{ow})	
- Automotive gasoline	2-7 (3)
- Aviation gasoline	2-6 (3)
Range of lowest credible toxicity data (mg l ⁻¹)	3.1-11.0 ¹
Toxicity	MODERATE/HIGH
BCF range	-
Bioaccumulation potential	LOW ²
Persistence: 50% removal of product mass ³	Approx 5 hours
100% removal of product mass	Approx 3 weeks

References

1 IARC (1989) 2 OHM/TADS (1985) 3 CONCAWE (1992)

Notes

1 Data reported as Loading Rates in terms of WAFs

2 Based on rapid volatilisation of water soluble, bioavailable hydrocarbons under field conditions

3 For removal of WHOLE product. 50% removal does NOT equal time taken for removal of 50% of total number of hydrocarbon constituents in the whole product. In general, this will be much shorter for lighter products such as gasoline and kerosine, whose chief constituents are very volatile hydrocarbons. Volatilisation will depend on quantity spilled and environmental conditions such as wind speed, temperature, wave action, etc.

A1.1 Description

Commonly known as “petrol” in the UK, gasoline is an extremely important energy source and is the primary product of most petroleum refineries. Gasolines are complex mixtures of volatile hydrocarbons with boiling points of around 30-220 °C and consisting of nearly 280 compounds in the C₄-C₁₂ range (CONCAWE 1992). They are produced by blending various refinery streams to meet required performance specifications. Such streams are derived from several sources, including light naphtha from atmospheric distillation, catalytic/thermal cracking processes, catalytic reforming and hydrotreatment. Many European gasolines also contain blending components of non-petroleum origin, especially oxygenates (mainly ethers and alcohols such as MTBE and TBA).

The hydrocarbon composition of a gasoline can vary widely depending on the type and nature of the crude processed, the refinery processes available, the process conditions, the overall balance of demand between gasoline and the other refinery products and product specifications (CONCAWE 1992). Gasolines typically consist of alkanes, cycloalkanes, aromatics and alkenes, in varying proportions depending on intended fuel use (see Section A1.2). Aromatic hydrocarbons (most importantly benzene, toluene, ethylbenzene and xylene) account for 87-95% of the water soluble fraction (WSF), while the most prevalent diaromatics are naphthalene and the methylnaphthalenes (CONCAWE 1992). Therefore, evaluation of the aquatic toxicity of gasolines is essentially an assessment of the toxicity of benzene, toluene, ethylbenzene and xylene, with some impact also exerted by the less soluble diaromatics which are present in the WSF at lower concentrations (CONCAWE 1992).

Additives may also be used in gasolines to improve certain performance features. For example, lead alkyls can be used to meet octane requirements, but an increasing proportion of gasolines are now unleaded. The upper permissible lead limit as set by the EU is 13 mg l⁻¹ in unleaded gasolines. Other additives can include anti-knock agents, anti-oxidants, corrosion inhibitors, metal de-activators, combustion chamber scavengers, detergents, de-icers and dyes. In general low concentrations of these additives are used; well below 0.1% by weight (CONCAWE 1992). The specific identity of additives tends to be proprietary information of the individual supplier.

In this profile data are provided for “whole” gasoline products and for the various refinery streams used in gasoline blending (i.e. light straight-run naphtha, isomate, alkylate, catalytically-cracked, etc).

A1.2 Uses

Gasolines are primarily used in internal combustion engines to power passenger cars and other types of vehicles including buses, trucks, motorbikes and aircraft, and can broadly be divided into two use categories; automotive gasoline and aviation gasoline (IARC 1989). Use and composition of each product type are discussed below.

A1.2.1 Automotive gasoline

Automotive gasoline is a complex inflammable mixture of volatile hydrocarbons, with or without additives, obtained by blending appropriate refinery streams to form a fuel suitable for use in spark ignition engines. It is used almost exclusively as a fuel for internal combustion

engines. Typical hydrocarbon composition of automotive gasolines by percentage volume, is as follows: alkanes (30-90), cycloalkanes (1-35), aromatics (5-55) and alkenes (0-20) (CONCAWE 1992).

A1.2.2 Aviation gasoline

This category covers all special grades of gasoline for use in aviation reciprocating engines. Many gasoline requirements of the automotive engine are shared by gasoline powered aviation engines. Typical hydrocarbon composition of aviation gasolines by percentage volume, is as follows: alkanes (75-100), cycloalkanes (0-1) and aromatics (0-25) (CONCAWE 1992). However, because aviation gasolines may be subjected to low temperatures in high-altitude flight, the freezing-point of the fuel cannot be above -58°C . Therefore, only three additives are permitted in aviation gasoline: dye, tetraethyl lead (used at higher levels than in automotive gasolines) and antioxidant (IARC 1989).

A1.2.3 Light Boiling Point Naphthas

It should be noted that this refinery stream (also referred to as straight-run naphthas) used in the blending of gasolines, also finds some use in the production of hydrocarbon solvents (D. Short CONCAWE, Pers. Comm. 1996).

A1.3 Production/consumption

The International Energy Agency (1987, cited in IARC 1989) reported total figures (1985) for gasoline production and consumption in OECD countries of 445 934 and 459 438 thousand tonnes, respectively. Corresponding figures of 99 569 and 91 081 were reported for Europe. These values are supported by CONCAWE (1992) who report that annual gasoline consumption in Europe is over 100 000 thousand (100 million) tonnes. A figure of 27 792 thousand tonnes has been reported for UK production in 1992 (Betton 1994), equal to 32.5% of all products produced from crude oil.

A1.4 Routes of entry to the aquatic environment

The main route of gasoline entry to the aquatic environment is likely to be as a result of accidental spillage of automotive and (to a much lesser extent) aviation fuel, during storage and transport. Accidents involving road tankers and ruptured pipelines are a particularly significant source of gasoline input to surface waters. In addition, leaks from corroded underground storage tanks can cause widespread contamination of groundwaters and, potentially, surface waters (see Section A1.6). A smaller quantity is expected to be lost to the environment through the actual use of gasoline in internal combustion engines.

A1.5 Reported environmental concentrations

As discussed in Section A1.6, differences in properties of individual hydrocarbon constituents of gasolines (i.e. solubility, vapour pressure, etc), along with various “weathering” processes, lead to very rapid changes in the relative concentrations of hydrocarbons, following a spill to surface water. It is probably for this reason that there are no reported concentrations of gasoline as a whole product in aquatic environments, even in terms of total gasoline hydrocarbons in the WSF (D. Short, CONCAWE, Pers. Comm., 1996).

Nevertheless, the following incidents give an indication of the magnitude of gasoline spillages that can occur. In 1978, 2,600,000 litres (1,900 tonnes) were spilled into Block Sound (USA) following the grounding of an ocean barge. No effects were apparent on resident biota (IARC 1989, D. Short, CONCAWE, Pers. Comm. 1996). In contrast, following a spill of 2000-3000 tonnes into the enclosed bays of Milford Haven (UK), large numbers of dead sea urchins were observed along with a number of other benthic organisms (limpets, winkles, mussels and whelks). Recovery was apparent after 1 year. Similarly, a 19 000 litres spill (13.8 tonnes) of aviation gasoline into a US stream caused extensive toxicity to fish and invertebrates. In Northern Idaho (US) 100 000 litres (72.6 tonnes) of gasoline were released to a small creek (D. Short, CONCAWE, Pers. Comm. 1996).

Groundwater contamination from underground storage tanks also appears to be a serious problem. In the US, 85% of underground storage tanks at petrol stations are made of steel that have no protection against corrosion. In New Jersey, more than 1400 incidents of leaking storage tanks were reported in 1978, leading to a total spillage of 4.2 million litres (3051 tonnes) (IARC 1989).

A1.6 Fate, behaviour and persistence in the aquatic environment

Gasolines are comprised of a great many hydrocarbons of predominantly 4 to 12 carbon atoms. Over this range there are considerable variations in vapour pressure and solubility properties. As a result, individual components will volatilise and solubilise at different rates and to differing extents. Thus, once spilt into surface waters, gasoline will not exist as such for very long. Moreover, due to the occurrence of these hydrocarbons in numerous substances, some of natural origin, there is often no way to link the presence of individual hydrocarbons to a particular source or spill.

Following a spillage of gasoline to the aquatic environment, the predominant removal route of many hydrocarbons will be by volatilisation to the atmosphere. Under laboratory conditions, gasoline has been reported to volatilise to 50% of its initial weight in just 2 hours and to 20% in 6-8 hours. The monoaromatic fraction is usually volatilised by >95% within 24 hours (CONCAWE 1992). Along with volatilisation, dissolution into the water column, photo-oxidation, biodegradation and adsorption to suspended particulate matter will also contribute to the weathering process of gasoline. The aromatic fraction (e.g. benzene, toluene, ethylbenzene and xylene) is of greatest concern due to its relatively high solubility and acute toxicity.

In a laboratory study, 25% of added gasoline was recovered from a sterile system as compared with only 3% in a biologically active system, following 58 hours incubation (CONCAWE 1992). This demonstrates that while volatilisation is probably responsible for most gasoline removal following a spillage, biodegradation contributes to total removal of hydrocarbons from the water column.

Horowitz and Atlas (1977) also found that biodegradation of spilt gasoline occurs under field conditions. Following a spill of 200 000 litres (145 tonnes) from a pipeline break to a nearby lake, the authors measured a substantial increase in hydrocarbon degrading micro-organisms in the sediments and water column of the contaminated area. 85% loss of gasoline was recorded after three weeks, with an additional 5% loss observed over the next two weeks.

A1.7 Toxicity to aquatic organisms

Interpretation of the available toxicity dataset for gasolines and their blending components (i.e. refinery stream naphthas) is complicated by the variety of test methodologies used in its generation. Many data are derived from studies in which the Water Soluble Fraction (WSF) was used, with toxicity measured either as mg l^{-1} of soluble hydrocarbons, or as the percentage dilution of the stock WSF. In addition data are also available from studies in which oil-in-water (OWD) dispersions were tested. However, the WSF method assumes that organisms are exposed only to truly dissolved hydrocarbons and does not account for exposure to undissolved, dispersed oil droplets. Moreover, it is not possible to accurately correlate concentrations of hydrocarbons in the WSF with the amount of product that must be added to the exposure medium to produce the effect of concern. In addition, the use of OWDs is not considered to be a consistent method for determining intrinsic toxicity of whole petroleum products. Therefore, the most appropriate procedure for ecotoxicity testing of complex hydrocarbon mixtures is the Water Accommodated Fraction (WAF) method, whereby effect concentrations are expressed both in terms of the water soluble fraction plus hydrocarbons present as dispersed droplets. Moreover WAF results are expressed as consistent “loading rates” (i.e. amount of product added to the exposure medium causing an effect e.g. LL50) which makes determination of the intrinsic toxicity of a whole petroleum product more reliable. (CONCAWE 1994). These issues are discussed more fully in Section 6.1 of the main report.

Further complications arise in interpreting the toxicity dataset as a result of poor reporting of study details. For instance, the majority of published studies do not identify the type of gasoline tested or even provide distinguishing characteristics such as aromatic content or presence of lead alkyls. Nevertheless, the available data reported as WAFs in terms of loading rates indicate that gasoline is of moderate to high acute toxicity to aquatic organisms, with effect loads of 3.1, 7.6 and 11 mg l^{-1} reported for algae, crustaceans and fish, respectively. These values suggest that fish are less sensitive than algae and crustaceans and are supported by WAF data for various refinery streams used in gasoline blending, for which toxicity values range from 3.6-18.0 mg l^{-1} . The available WAF data are supported by L(E)C50s ranging from 1.8-6.3 mg l^{-1} measured as WSFs (see Table A1.2).

In addition, L(E)L50s as low as 82 and 170 mg l^{-1} have been reported for rainbow trout (*Oncorhynchus mykiss*) and the water flea (*Daphnia magna*), following exposure to gasolines as OWDs. These values are much lower than the WAF/WSF data as they were obtained in open studies in which exposure solutions were not renewed. Therefore, loss of the acutely toxic hydrocarbon constituents from the solutions by volatilisation, is likely to have led to a lower expression of toxicity.

Table A1.2 Aquatic toxicity of gasolines and some refinery streams used in blending

SPECIES	EXPOSURE DURATION	EFFECT	CONC (mg l ⁻¹)	COMMENTS	REF
Algae					
<i>Selenastrum capricornutum</i> (Green alga)	72 hours	IL50 (specific growth rate)	3.1	WAF, gasoline	1
<i>Selenastrum capricornutum</i> (Green alga)	72 hours	IL50 (specific growth rate)	3.6	WAF, light straight-run	1
Crustaceans					
<i>Daphnia magna</i> (Water flea)	48 hours	EL50 (immobility)	7.6	WAF, gasoline	1
<i>Daphnia magna</i> (Water flea)	48 hours	EL50 (immobility)	4.5	WAF, Light straight-run	1
<i>Daphnia magna</i> (Water flea)	48 hours	EL50 (immobility)	8.4	WAF, Light reformat	1
<i>Daphnia magna</i> (Water flea)	48 hours	EC50 (immobility)	3.0	WSF, gasoline	2
<i>Daphnia magna</i> (Water flea)	24 hours	EL50 (immobility)	170.0	OWD, gasoline	1
<i>Mysidopsis bahia</i> (Mysid shrimp)	96 hours	EC50	1.8	WSF, gasoline. Saltwater species	2
Fish					
<i>Oncorhynchus mykiss</i> (Rainbow trout)	96 hours	LL50	11.0	WAF, gasoline	1
<i>Oncorhynchus mykiss</i> (Rainbow trout)	96 hours	LL50	18.0	WAF, light-straight-run	1
<i>Oncorhynchus mykiss</i> (Rainbow trout)	96 hours	LL50	10.0	WAF, Isomerate	1
<i>Oncorhynchus mykiss</i> (Rainbow trout)	96 hours	LL50	12.0	WAF, light reformat	1
<i>Oncorhynchus mykiss</i> (Rainbow trout)	96 hours	LC50	2.7	WSF, gasoline	2
<i>Oncorhynchus mykiss</i> (Rainbow trout)	96 hours	LL50	82.0	OWD, gasoline	1

SPECIES	EXPOSURE DURATION	EFFECT	CONC (mg l ⁻¹)	COMMENTS	REF
<i>Lepomis macrochirus</i> (Bluegill sunfish)	96 hours	LC50	6.3	WSF, gasoline	2

Notes to Table A2.2:

- EL50 Median Effect Loading Rate
- IL50 Loading rate corresponding to 50% inhibition
- LL50 Median Lethal Loading Rate
- OWD Oil in Water Dispersion. In terms of mg of oil added to exposure medium (analogous to loading rate) (See Section 5.1)
- WAF Water Accommodated Fraction. In terms of mg of oil in the WSF (see below) plus mg in the form of undissolved, dispersed droplets following mixing and separation in the exposure medium (See Section 6.1)
- WSF Water Soluble Fraction. In terms of mg of total dissolved hydrocarbons in the WSF following mixing and separation of oil in the exposure medium (See Section 6.1)

References

- 1 D. Short (CONCAWE, Pers. Comm. 1996)
- 2 Cited in CONCAWE (1992)

A1.8 Bioaccumulation potential

Interpretation of bioaccumulation data of petroleum products in fish also presents some difficulties since each constituent compound bioaccumulates to the extent determined by its own physico-chemical properties and so each component ideally needs to be measured independently (CONCAWE 1992, see Section 6.1.2). Given the rapid removal of the water soluble hydrocarbons by volatilisation and biodegradation, bioaccumulation of gasoline is expected to be minimal or non-existent under field conditions (CONCAWE 1992). However, there are no laboratory data available to confirm the intrinsic bioaccumulation potential of water soluble gasoline hydrocarbons, in where studies where exposure concentrations are maintained.

A2 KEROSESINES

Table A2.1 Summary of data for kerosine products

Carbon range	C ₉ -C ₁₆ (1)
Appearance	Yellow-white liquid. Will float as a slick on water surfaces (4)
Uses	Aviation fuel, heating oil, solvent
Boiling point range (°C)	
- Straight-run kerosine	125-292 (1)
- Hydrodesulphurized kerosine	175-284 (1)
Flash point (°C)	
- US straight-run kerosine	62 (1)
- Hydrodesulphurized kerosine	60 (1)
- European kerosines	40-45 (1)
- Civil fuel Jet A and military fuel JP-8	38 (2)
- Military fuels JP-5 and JP-7	60 (2)
- Fuel Oil No 1	38 (2)
Freezing point (°C)	-57-48 (for various jet fuels) (1)
Density (g cm ⁻³)	0.82 (3)
Vapour pressure (hPa)	10-210 (3)
Octanol-water partition coefficient (log K _{ow})	
- Straight-run kerosine	3.3-6+ (1)
- Hydrodesulphurized kerosine	3.3-6+ (1)
Range of lowest credible toxicity data (mg l ⁻¹)	1.4-18.0 ¹
Toxicity	MODERATE/HIGH
BCF range	88-159
Bioaccumulation potential	LOW
Persistence: 50% removal of product mass ²	Approx 1 day
100% removal of product mass	Approx 8 months

References

- 1 CONCAWE (1994) 2 IARC (1989) 3 Short (CONCAWE, Pers. Comm. 1996)
 4 OHM/TADS (1985)

Notes

- 1 Data reported as Loading Rates in terms of WAFs
 2 For removal of WHOLE product. 50% removal does NOT equal time taken for removal of 50% of total number of hydrocarbon constituents in the whole product. In general, this will be much shorter for lighter products such as gasoline and kerosine, whose chief constituents are very volatile hydrocarbons. Volatilisation will depend on quantity spilled and environmental conditions such as wind speed, temperature, wave action, etc.

A2.1 Description

Kerosine is the generic name for the lighter end of a group of petroleum substances known as middle distillates, the heavier end being the gas oils (see Section A3). Although kerosines are essentially of two types (“straight-run” and “cracked”), subsequent treatment often blurs this

simplistic distinction. Straight-run kerosine streams produced by the atmospheric distillation of crude oil are subsequently treated by processes such as desulphurisation and hydrogenation to produce kerosines suitable for blending as jet fuels (CONCAWE 1994).

The major components of kerosines are branched and straight chain paraffins and naphthenes (cycloparaffins), which normally account for at least 70% by volume of a process stream. Aromatic hydrocarbons, mainly alkylbenzenes and alkyl naphthalenes do not normally exceed 25% by volume (CONCAWE 1994). The boiling range of kerosine fuel oils generally precludes the occurrence of substantial quantities of PAHs (IARC 1989).

Kerosines have relatively low water solubilities, but the fraction that is soluble is known to consist predominately of aromatic hydrocarbons such as benzene, toluene and xylene (CONCAWE 1988, 1994).

A2.2 Uses

A2.2.1 Jet fuel

The most important use of kerosines is in blending aviation fuels. Such fuels have demanding specifications, both for civil and military aircraft. In general there are three types of jet fuel, namely; kerosine type (kerosine blends), “wide cut” type (kerosine blended with low flash naphtha) and high flash point kerosine. Each type has varying performance properties and finds specific uses as fuels in either aviation, military or naval aircraft (CONCAWE 1994).

Jet fuels often contain additives such as antioxidants, metal deactivators, corrosion inhibitors, de-icers, static dissipators and biocides, to improve performance (CONCAWE 1994).

A2.2.2 Fuel oil

Kerosines are also used as domestic and industrial heating fuels (see Section A3.2 for a more detailed description of these uses). In the US such heating oils are marketed as Fuel Oil No 1 (IARC 1989) and may be straight-run distillates or blends of straight-run and cracked streams. However, the use of kerosine as a heating oil has declined substantially and is now used far less for this purpose than Fuel Oil No 2 (diesel fuel oil, see Section A3.2), although kerosine still has some residential and farm uses as a heating fuel oil (IARC 1989).

As with jet fuels, additives are also used with kerosine in Fuel Oil No 1 and can include antioxidants, dispersants and corrosion inhibitors (CONCAWE 1994).

A2.2.3 Solvents

Kerosines also find some use as solvents in the formation of a wide range of products including cleaning formulations, insecticides, anti-foams, and mould release agents. The kerosines used in these products are often of a narrower distillation range than those used in fuels and are often further treated to reduce odour and aromatics content (CONCAWE 1994).

A2.3 Production/consumption

The International Energy Agency (1987, cited in IARC 1989) reported total figures (1985) for jet fuel production and consumption in OECD countries of 90,280 and 88,880 thousand

tonnes, respectively. Corresponding figures of 24,376 and 22,787 were reported for Europe. A figure of 9 618 thousand tonnes has been reported for UK production in 1992 (Betton 1994), equal to 11.5% of all products produced from crude oil.

A2.4 Routes of entry to the aquatic environment

The main route of kerosine entry to the aquatic environment is likely to be as a result of accidental spillage of aviation fuel and heating oil (i.e. Fuel Oil No 1) during storage, transport and use. In addition, it is common practice for aircraft to jettison excess fuel in the air under some conditions (IARC 1989).

A2.5 Reported environmental concentrations

In 1982, a leak from a petroleum pipeline contaminated the catchment of a small trout stream in the US with an estimated 1 310 barrels of aviation kerosine (Guiney *et al* 1987). The highest concentration of total kerosine range hydrocarbons detected following this leak was 33.2. mg l⁻¹ in a small spring. This site contained by far the highest concentrations as it received kerosines leached from the surrounding soil. Concentrations at other sampling sites in the month following the spill were around 0.5-1.0 mg l⁻¹.

The following incidents give an indication of the magnitude of kerosine spillages that can occur. In 1975, 83 000 gallons (314 000 l) of JP-4 jet fuel were spilled in the US, while in 1971 14 tonnes of jet fuel JP-5 (in a mixture with Fuel Oil No 2) were spilled from a US storage facility (IARC 1989).

A2.6 Fate, behaviour and persistence in the aquatic environment

Following a spillage of kerosine to the aquatic environment, most of the constituent hydrocarbons will evaporate and photodegrade in the atmosphere, with half-lives of less than a day (CONCAWE 1994). However, the less volatile hydrocarbons will persist in aquatic ecosystems for longer periods, where they remain floating on the surface of water, although some hydrocarbons will adsorb to suspended solids and settle in sediments where they may be particularly persistent (CONCAWE 1994).

Very few studies have been published concerning the biodegradation of kerosines and none are known that have used the standard OECD 28 day test. In the presence of nutrient salts, Biochemical Oxygen Demand (BOD) values 41% and 36% of the theoretical values (ThOD) have been reported for kerosine in fresh and saltwater, respectively, following 5 days incubation (CONCAWE 1994). Moreover, in the absence of nutrient salts, the saltwater 5 day BOD was only 2% of the ThOD and had not increased after 10 days. These data indicate that kerosine is unlikely to be readily biodegraded in the aquatic environment.

The persistence of kerosine range hydrocarbons in surface waters is supported by a field study conducted by Guiney *et al* (1987) in which the disappearance of kerosine was monitored at various sites on a catchment contaminated by jet fuel as a result of a pipeline leak. In this study the authors distinguished hydrocarbons arising from weathered kerosine from “background” hydrocarbons, by measuring hydrocarbons present in samples taken at control sites. The highest concentration of total kerosine range hydrocarbons detected was 33.2. mg l⁻¹ in a small spring. This site contained by far the highest concentrations as it received kerosines

leached from the surrounding soil. Concentrations at other sampling sites in the month following the spill were around 0.5-1.0 mg l⁻¹. These concentrations generally declined to background levels over a period of 4 to 8 months, although concentrations of up to 18 mg kg⁻¹ remained in sediments 14 months after the spill. Sediment concentrations had returned to normal around two years after the spill. The spill caused acute lethality to resident aquatic life in the stream.

A2.7 Toxicity to aquatic organisms

Interpretation of the available toxicity dataset for kerosine is complicated by the variety of test methodologies used in its generation. Most data are derived from studies in which the Water Soluble Fraction (WSF) was used, with toxicity measured either as mg l⁻¹ of soluble hydrocarbons, or as the percentage dilution of the stock WSF. However, this method assumes that organisms are exposed only to truly dissolved hydrocarbons and does not account for exposure to undissolved, dispersed oil droplets. Moreover, it is not possible to accurately correlate concentrations of hydrocarbons in the WSF with the amount of product that must be added to the exposure medium to produce the effect of concern. In addition, the use of OWDs is not considered to be a consistent method for determining intrinsic toxicity of whole petroleum products. Therefore, the most appropriate procedure for ecotoxicity testing of complex hydrocarbon mixtures is the Water Accommodated Fraction (WAF) method, whereby effect concentrations are expressed both in terms of the water soluble fraction plus hydrocarbons present as dispersed droplets. Moreover WAF results are expressed as consistent “loading rates” (i.e. amount of product added to the exposure medium causing an effect e.g. LL50) which makes determination of the intrinsic toxicity of a whole petroleum product more reliable. (CONCAWE 1994). These issues are discussed more fully in Section 6.1 of the main report.

The available data reported as WAFs in terms of loading rates indicate that kerosine is of moderately high acute toxicity to aquatic organisms, with effect loads ranging from 1.4-8.3 mg l⁻¹ for algae and crustaceans and LL50s of 13.5-25.0 mg l⁻¹ for fish. These values suggest that fish are less sensitive than algae and crustaceans and are supported by respective L(E)C50s (as WSFs) of 3.1 and 5.6-18.0 mg l⁻¹ (CONCAWE 1994, 1996. see Table A2.2). The lower toxicity of the “sweetened” kerosine to *D. magna* is a result of losses through volatilisation either during the test or during sampling and analysis (CONCAWE 1996).

Table A2.2 Aquatic toxicity of kerosines

SPECIES	EXPOSURE DURATION	EFFECT	CONC (mg l ⁻¹)	COMMENTS	REF
Algae					
<i>Selenastrum capricornutum</i> (Green alga)	72 hours	IL50 (specific growth rate)	3.7	WAF, sweetened	1
			8.3	Hydrodesulphurised	
		NOEL	6.7	Hydrocracked	
			0.2	WAF, sweetened	1
			4.0	Hydrodesulphurised	
		6.0	Hydrocracked		

SPECIES	EXPOSURE DURATION	EFFECT	CONC (mg l ⁻¹)	COMMENTS	REF
Crustaceans					
<i>Daphnia magna</i> (Water flea)	48 hours	EL50 (immobility)	21.0	WAF, sweetened	1
			1.4	Hydrodesulphurised	
		1.9	Hydrocracked		
		NOEL	0.9	WAF, sweetened	
		-	Hydrodesulphurised		
0.3	Hydrocracked				
<i>Chaetogammarus marinus</i>	96 hours	LL50	1.4	WAF, Hydrocracked.	2
		NOEL	1.0	Saltwater species	
<i>Daphnia magna</i> (Water flea)	48 hours	EC50	3.1	WSF, Jet Fuel JET-A	2
Fish					
<i>Oncorhynchus mykiss</i> (Rainbow trout)	96 hours	LL50	18.0	WAF, sweetened	1
			25.0	Hydrodesulphurised	
		NOEL	20.0	Hydrocracked	
		4.5	WAF, sweetened		
		6.8	Hydrodesulphurised		
1.4	Hydrocracked				
<i>Brachydanio rerio</i> (Zebrafish)	96 hours	LL50	13.5	WAF, Hydrocracked	2
		NOEL	5.6		
<i>Pimephales promelas</i> (Fathead minnow)	96 hours	LC50	5.5	WSF, Jet Fuel JP-8	2
		LC50	18.0	WSF, Jet Fuel JP-4	

Notes to Table A2.2:

EL50 Median Effect Loading Rate

IL50 Loading rate corresponding to 50% inhibition

LL50 Median Lethal Loading Rate

NOEL No-Observed Effect Loading Rate

WAF Water Accommodated Fraction. In terms of mg of oil in the WSF (see below) plus mg in the form of undissolved, dispersed droplets following mixing and separation in the exposure medium (See Section 6.1)

WSF Water Soluble Fraction. In terms of mg of total dissolved hydrocarbons in the WSF following mixing and separation of oil in the exposure medium (See Section 6.1)

References

1 CONCAWE (1996)

2 Cited in CONCAWE (1994)

A2.8 Bioaccumulation potential

Interpretation of bioaccumulation data of petroleum products in fish also presents some difficulties since each constituent compound bioaccumulates to the extent determined by its own physico-chemical properties and so each component ideally needs to be measured independently (CONCAWE 1992, see Section 6.1.2). However, available BCFs indicate that kerosine hydrocarbons do not accumulate to particularly high concentrations and are readily depurated following transfer of organisms to contaminant-free water.

For example, Bioconcentration Factors (BCFs) of 159 and 88 have been reported for American flagfish (*Jordonella floridae*) and rainbow trout (*O. mykiss*) following exposure to jet fuel (JP-8) concentrations of 1-6.8 and 1.4-8.0 mg l⁻¹ (WSF) over 128 and 112 days, respectively (Klein and Jenkins 1983). In another study by the same authors, a BCF of 130 was reported for *J. floridae* following 112 days exposure to a single WSF containing 2.5 mg l⁻¹ of dissolved hydrocarbons. Following removal to clean water, 90% elimination of the accumulated hydrocarbons was observed over 14 days.

A3 DISTILLATE FUEL OILS (LIGHT FUEL OILS OTHER THAN KEROSENE) AND COMPONENT GAS OILS

Table A3.1 Summary of data for Fuel Oil No 2, automotive diesel fuel and component gas oils

Carbon range	
- Fuel Oil No 2	C ₁₁ -C ₂₀ (1)
- Component Gas Oils	C ₉ -C ₂₅ (2)
Appearance	Yellow liquid. Will float as a slick on water surfaces (3)
Uses	Heating fuel, automotive fuel
Boiling point range (°C)	
- Fuel Oil No 2	160-400 (2)
- Automotive diesel	160-390 (2)
- Straight-run distillate component gas oil	185-391 (2)
Flash point (°C)	
- Fuel Oil No 2	56 (2)
- Automotive diesel	56 (2)
Freezing point (°C)	No data
Density (g cm ⁻³)	
- Fuel Oil No 2	0.81-0.9 (2)
- Automotive diesel	0.81-0.9 (2)
- Straight-run distillate component gas oil	0.84 (2)
Vapour pressure (hPa) @ 40 °C	
- Fuel Oil No 2	4 (2)
- Automotive diesel	4 (2)
Octanol-water partition coefficient (log K _{ow})	
- Straight-run kerosine	3.9-6+ (2)
- Hydrodesulphurized kerosine	3.9-6+ (2)
Range of lowest credible toxicity data (mg l ⁻¹)	2.6-21.0
Toxicity	MODERATE - HIGH
BCF range	8.5 ³
Bioaccumulation potential	LOW
Persistence: 50% removal of product mass ²	Approx 6 months
100% removal of product mass	Approx 2 years

References

1 IARC (1989) 2 Short (CONCAWE, Pers. Comm. 1996) 3 OHM/TADS (1985)

Notes

1 Data reported as Loading Rates in terms of WAFs

2 For removal of WHOLE product. i.e. 50% removal does NOT equal time taken for removal of 50% of total number of hydrocarbon constituents in the whole product.

3 One value only

A3.1 Description

Because of the methods employed in their production, fuel oils fall into two broad categories: distillates (light) and residuals (heavy). The distillates consist of distilled process streams, while the residual fuel oils are residues remaining after distillation. The American Society for Testing and Materials (ASTM) define the distillate products as Fuel Oil Nos 1 and 2, while Nos 4, 5 and 6 include the residual (heavy) fuel oils (IARC 1989). The residual fuel oils are reviewed separately in Section A4.

Distillate fuel oils are complex mixtures of hydrocarbons that also contain minor amounts of sulphur, nitrogen and oxygen-containing molecules. They contain normal and branched alkanes, cycloalkanes (naphthenes), aromatics and partially reduced aromatics. Fuel Oil No 1 spans the approximate carbon range C₉-C₁₆, while Fuel Oil No 2 spans the range C₁₁-C₂₀ (IARC 1989). The latter product is blended from gas oil components produced by atmospheric distillation, vacuum distillation of atmospheric residue and/or by cracking processes (D. Short, CONCAWE, Pers. Comm. 1996).

Fuel Oil No 2 contains less than 5% three to seven-ringed polycyclic aromatic hydrocarbons (PAHs). Typical PAH concentrations in a No 2 fuel oil sample might be 0.6, 37, 429 and 7677 mg l⁻¹ for benzo(a)pyrene, fluoranthene, phenanthrene and 2-methylphenanthrene (cited in IARC 1989). For a detailed review of the relative environmental hazards posed by PAHs see the corresponding WRc report for these compounds (Grimwood 1996).

Distillate fuel oils may also contain additives that serve as antioxidants, dispersants and corrosion inhibitors (IARC 1989).

A3.2 Uses

In general, “distillate fuel oils” are used as burner fuel for domestic and industrial heating and for raising steam in the generation of electricity. However, the basic physico-chemical properties of Fuel Oil Nos 1 and 2 as used for heating purposes, are very similar to the kerosine and diesel fuels used for aviation and road transport, respectively. The final products are treated as required for a particular application and may contain additives that are specific for the intended use, but they are otherwise virtually indistinguishable (IARC 1989). Therefore, Fuel Oil No 1 is not considered further in this section as its properties are covered in Section A2 (“Kerosines”). The rest of this section concentrates on Fuel Oil No 2 and European automotive diesel fuel. Since both these products are blended from component gas oils with similar properties, where appropriate, data relating to these components are also provided.

A3.2.1 Fuel Oil No 2

Fuel Oil No 2 is a heavier distillate than Fuel Oil No 1. It is intended for use in atomizing type burners which spray the oil into a combustion chamber where the droplets burn while in a suspension. This grade of oil is used in most home heating installations and in many medium capacity commercial or industrial burners (IARC 1996).

A3.2.2 Automotive diesel fuel

In the US, diesel fuel oils are classified as Nos 1, 2 and 3. Diesel Fuel No 2 is equivalent to European automotive diesel fuel (similar in properties to Fuel Oil No 2), whereas Diesel Fuel Nos 1 and 4 are essentially equivalent to kerosine (Fuel Oil No 1) and Fuel Oil No 4 (IARC 1989). Information relating to the latter two products are included in the sections covering “kerosines” (A2) and “residual fuel oils” (A4), respectively.

Automotive diesel fuel is chiefly used in heavy transportation services such as trains, trucks, busses and river boats, although it is finding increasing use in private vehicles.

A3.3 Production/consumption

Production/consumption figures specifically relating to Fuel Oil No 2 and automotive diesel fuel do not appear to be available. However, IARC (1989) report that Fuel Oil No 2 is used far more widely for heating purposes than Fuel Oil No 1 (kerosine), although the use of both products for heating has declined, with transportation finding the greatest use. In 1983 estimated consumption of distillate fuel oils (i.e. Nos 1 and 2) in the US was 422 322 barrels for all heating purposes and 540 403 barrels for transportation (IARC 1989). A more meaningful figure of 26 057 thousand tonnes has been reported for UK automotive diesel production in 1992 (Betton 1994), equal to 30.5% of all products produced from crude oil.

A3.4 Routes of entry to the aquatic environment

The main route of entry to the aquatic environment of these petroleum products is likely to be as a result of accidental spillages during storage, transport and use, particularly road run-off of automotive diesel fuels and direct input to surface water from motor boats.

A3.5 Reported environmental concentrations

There appear to be no available data specifically relating to measured concentrations of diesel fuel hydrocarbons in aquatic ecosystems. However, the following incidents give an indication of the magnitude of spillages that can occur. In 1987, 11.4 million litres of Fuel Oil No 2 were spilt in the US following the rupture of a storage tank, while in 1969, 700 000 litres of Fuel Oil No 2 were released after the grounding of a barge (cited in IARC 1989).

A3.6 Fate, behaviour and persistence in the aquatic environment

On entering aquatic ecosystems, the lighter hydrocarbons in gas oils, Fuel Oil No 2 and automotive diesel fuel will generally volatilise but, depending on circumstances, the remainder will become dispersed in the water column or adsorbed to suspended solids and, subsequently, to benthic sediments (D. Short, CONCAWE, Pers. Comm. 1996). This is supported by the work of Lee and Takahashi (1977) who found that the volatile components of Fuel Oil No 2 (e.g. benzene, toluene and xylene) were volatilised very rapidly from saltwater mesocosms, with complete removal of a benzene concentration of 0.1 mg l⁻¹ in just 2 days. In this study, the authors identified the main non-volatile hydrocarbons as naphthalene, methylnaphthalenes and dimethylnaphthalenes.

Gearing *et al* (1980) also conducted saltwater mesocosm studies in which the fate of total hydrocarbon concentrations of 0.093-0.18 mg l⁻¹ derived from the addition of Fuel Oil No 2 were monitored. The results suggest that the hydrocarbons in the water adsorb to suspended solids in inverse proportion to their degree of aqueous solubility. This process fractionates the oil and the eventual settling of the particulate matter carries to the sediment around 50% of the relatively insoluble, saturated hydrocarbons, but less than 20% of the relatively soluble aromatic hydrocarbons.

There are no available data on the behaviour of these products in standard tests for biodegradability. However, under aerobic conditions the lower molecular weight constituents may be biodegraded relatively rapidly, although the higher molecular weight compounds (e.g. PAHs) will biodegrade more slowly. Under anaerobic conditions such as in anoxic sediments, biodegradation of gas oils and their products is likely to be negligible and the products may persist for years (D. Short, CONCAWE, Pers. Comm. 1996). Indeed, Gearing *et al* (1980) found that the persistent residue of branched alkanes, cycloalkanes and aromatics in the sediments of mesocosms following addition of Fuel Oil No 2, persisted for at least one year after the end of the experiment.

A3.7 Toxicity to aquatic organisms

Interpretation of the available toxicity dataset for Fuel Oil No 2, automotive diesel fuel and component gas oils is complicated by the variety of test methodologies used in its generation. Most data are derived from studies in which the Water Soluble Fraction (WSF) was used, with toxicity measured either as mg l⁻¹ of soluble hydrocarbons, or as the percentage dilution of the stock WSF. In addition data are also available from studies in which oil-in-water (OWD) dispersions were tested. However, the WSF method assumes that organisms are exposed only to truly dissolved hydrocarbons and does not account for exposure to undissolved, dispersed oil droplets. Moreover, it is not possible to accurately correlate concentrations of hydrocarbons in the WSF with the amount of product that must be added to the exposure medium to produce the effect of concern. In addition, the use of OWDs is not considered to be a consistent method for determining intrinsic toxicity of whole petroleum products. Therefore, the most appropriate procedure for ecotoxicity testing of complex hydrocarbon mixtures is the Water Accommodated Fraction (WAF) method, whereby effect concentrations are expressed both in terms of the water soluble fraction plus hydrocarbons present as dispersed droplets. Moreover WAF results are expressed as consistent “loading rates” (i.e. amount of product added to the exposure medium causing an effect e.g. LL50) which makes determination of the intrinsic toxicity of a whole petroleum product more reliable. (CONCAWE 1994). These issues are discussed more fully in Section 6.1 of the main report.

The available data reported as WAFs in terms of loading rates indicate that these products are of moderate to high acute toxicity to aquatic organisms, with effect loads ranging from 2.6-7.8, 20-32 and 7-21 mg l⁻¹ for algae, crustaceans and fish, respectively (see Table A3.2). The crustacean values are supported by a 48 hour WSF LC50 of 26.6 mg l⁻¹ and OWD values of 11-21 mg l⁻¹, although values as low as 0.9-3.5 (WSF) and 1.3-0.9 mg l⁻¹ (OWD) have been reported for certain saltwater species. The fish WAF values of 7-21 mg l⁻¹ are broadly supported by WSF and OWD LC50s of 35-93 and >6.9 7-21 mg l⁻¹, respectively.

There is some evidence to suggest that an increase in temperature increases toxicity of these petroleum products, probably as a result of increased uptake of dissolved hydrocarbons. This

is supported by 48 hour LC50s (WSFs) of 71.9, 26.6 and 9.7 7-21 mg l⁻¹ reported for the water flea (*Daphnia magna*), following exposure at 10, 20 and 25 °C, respectively (Ullrich and Milleman 1983).

Table A3.2 Aquatic toxicity of Fuel Oil No 2, automotive diesel and gas oil components

SPECIES	EXPOSURE DURATION	EFFECT	CONC (mg l ⁻¹)	COMMENTS	REF
Algae					
<i>R. subcapitata</i>	72 hours	EL50 (growth)	7.8	WAF, automotive diesel	1
			2.6	WAF, automotive diesel	
Crustaceans					
<i>Daphnia magna</i> (Water flea)	48 hours	EL50 (immobility)	32.0	WAF, automotive diesel	1
			20.0	WAF, automotive diesel	
<i>Daphnia magna</i> (Water flea)	48 hours	LC50	71.9	WSF (total organic carbon), automotive diesel. 10°C	2
			26.6	20°C	
			8.0	25°C	
<i>Mysidopsis alyra</i>	48 hours	LC50	0.9	WSF, No 2 Fuel Oil. Saltwater species	3
			1.3	OWD	
<i>Palaemonetes pugio</i>	96 hours	LC50	3.5	WSF, No 2 Fuel Oil. Saltwater species	3
			3.0	OWD	
<i>Crangon crangon</i> (Brown shrimp)	96 hours	LC50	11.0	OWD, Gas Oil	1
			21.0	OWD, automotive diesel	
Fish					
<i>Brachydanio rerio</i> (Zebra fish)	96 hours	LL50	7.0	WAF, Steam cracked gas oil	1
<i>Oncorhynchus mykiss</i> (Rainbow trout)	96 hours	LL50	21.0	WAF, automotive diesel	1
<i>Cyprinodon variegatus</i> (Sheepshead minnow)	96 hours	LC50	>6.9	WSF, No 2 Fuel Oil. Saltwater species	4
			93.0	OWD	
<i>Pimephales promelas</i>	96 hours	LC50	35.0	OWD, No 2 Fuel Oil	5

SPECIES	EXPOSURE DURATION	EFFECT	CONC (mg l ⁻¹)	COMMENTS	REF
(Fathead minnow)					

Notes to Table A3.2:

- EL50 Median Effect Loading Rate
- LL50 Median Lethal Loading Rate
- NOEL No-Observed Effect Loading Rate
- OWD Oil in Water Dispersion. In terms of mg of oil added to exposure medium (analogous to loading rate) (See Section 5.1)
- WAF Water Accommodated Fraction. In terms of mg of oil in the WSF (see below) plus mg in the form of undissolved, dispersed droplets following mixing and separation in the exposure medium (See Section 6.1)
- WSF Water Soluble Fraction. In terms of mg of total dissolved hydrocarbons in the WSF following mixing and separation of oil in the exposure medium (See Section 6.1)

References

- 1 D. Short (CONCAWE , Pers. Comm. 1996)
- 2 Ullrich and Milleman (1983)
- 3 Anderson *et al* (1974b)
- 4 Anderson *et al* (1974a)
- 5 Hedtke and Puglisi (1982)

A3.8 Bioaccumulation potential

Interpretation of bioaccumulation data of petroleum products in fish also presents some difficulties since each constituent compound bioaccumulates to the extent determined by its own physico-chemical properties and so each component ideally needs to be measured independently (CONCAWE 1992, see Section 6.1.2). Available data concerning the bioaccumulation of either Fuel Oil No 2, automotive diesel fuel or component gas oils is extremely limited. The highest BCF reported is one of just 8.5 for the clam following 1 weeks exposure to an emulsion containing 10 mg l⁻¹ of Fuel Oil No 2 (D. Short, CONCAWE, Pers. Comm. 1996). In addition, it has been reported that oysters (*Crassostrea virginica*) accumulate Fuel Oil No 2 to a peak concentration 100 hours after initial exposure, at which time the hydrocarbons are rapidly depurated (D. Short, CONCAWE, Pers. Comm. 1996). This is supported by the results of a study in which brown shrimp (*Penaeus aztecus*) were exposed to a 30% WSF of Fuel oil No 2 (Anderson *et al* 1974a). In this test, the naphthalenes were the most accumulated hydrocarbons, with methylnaphthalenes being accumulated to a considerably greater extent than either naphthalene or dimethylnaphthalenes. Following removal to clean seawater, the tissue concentrations of these aromatics decreased to undetectable levels in just 10 hours.

The limited data therefore indicate that water soluble diesel hydrocarbons are not accumulated to high concentrations and are readily depurated from the tissues of aquatic biota. However, it should be noted that BCFs for individual compounds may be higher as indicated by the high partition coefficients of these compounds (log Kow 4->6). More measured data on complex diesel mixtures are required, to fully assess the bioaccumulation potential of this product.

A4 RESIDUAL FUEL OILS (HEAVY FUEL OILS)

Table A4.1 Summary of data for residual fuel oils

Carbon range	Up to C ₅₀ (1)
Appearance	Dark viscous liquids. Will float as slicks on water surfaces (2)
Uses	
- Fuel Oil No 4	Heating fuel, automotive fuel (trains, boats, stationary engines)
- Fuel Oil No 5	Heating fuel
- Fuel Oil No 6	Heating fuel
Boiling point range (°C)	
- Fuel Oil No 4	No data
- Fuel Oil No 5	No data
- Fuel Oil No 6	150-600 (1), 400 (2)
Flash point (°C)	
- Fuel Oil No 4	55 (3)
- Fuel Oil No 5	55 (3)
- Fuel Oil No 6	60 (3)
Freezing point (°C)	No data
Density (g cm ⁻³)	
- Fuel Oil No 4	No data
- Fuel Oil No 5	No data
- Fuel Oil No 6	1.01-1.07 (1)
Vapour pressure (hPa) @ 20 °C	
- Fuel Oil No 4	No data
- Fuel Oil No 5	No data
- Fuel Oil No 6	>5 (1)
Octanol-water partition coefficient (log K _{ow})	
- Fuel Oil No 4	No data
- Fuel Oil No 5	No data
- Fuel Oil No 6	2.7-6+ (1)
Range of lowest credible toxicity data (mg l ⁻¹)	0.9-3.1
Toxicity	MODERATE/HIGH
BCF range	20 ²
Bioaccumulation potential	LOW
Persistence: 50% removal of product mass ³	Approx 2 years
100% removal of product mass	Approx 6 years

References

1 Short (CONCAWE, Pers. Comm. 1996) 2 OHM/TADS (1985) 3 IARC (1989)

Notes

1 Data reported as Loading Rates in terms of WAFs

2 One value only

3 For removal of WHOLE product. i.e. 50% removal does NOT equal time taken for removal of 50% of total number of hydrocarbon constituents in the whole product.

A4.1 Description

Residual fuel oils are derived from residues remaining after the distillation process that produces distillate fuel oils (see Sections A2 and A3). The American Society for Testing and Materials (ASTM) define residual products as Fuel Oil Nos 4, 5 and 6 (IARC 1989). Fuel Oil Nos 5 and 6 are also known as Navy Fuel Oil and Bunker C Fuel Oil, respectively, while Fuel Oil No 4 is essentially equivalent to Diesel Fuel No 4 (IARC 1989, OHM/TADS 1985). Fuel Oil Nos 5 and 6 are clearly heavy, residual products. However, while Fuel Oil No 4 is usually a “light” residual, it sometimes is, or contains, a heavy distillate and so is often referred to as “distillate marine fuel oil” (IARC 1989).

The principal manufacturing process of residual fuel oils generally involves the addition of low viscosity blending stocks (typically Fuel Oil No 2) to high viscosity residues in the proportions necessary to meet the viscosity specifications desired. The high viscosity residues typically derive from atmospheric and vacuum distillation, or from thermally cracked residues. This process leads to the production of highly complex mixtures of high molecular weight compounds which are difficult to characterise in detail. Since they are blended from fractions with boiling points between 350 and 650 °C, the molecular weights of the constituents can span the range from around 300 to greater than 1000. Generic types include asphaltenes, polar aromatics, naphthalene aromatics, aromatics, saturated hydrocarbons and heteromolecules containing sulphur, oxygen, nitrogen and metals (e.g. nickel and vanadium) (IARC 1989).

In addition, appreciable concentrations of PAHs are generally present in residual fuels. The specific PAHs and concentrations at which they are present in a residual product will depend on the nature and quantity of the low viscosity blending stocks and relative proportions of virgin and cracked residues used in its manufacture. If the blending stocks are predominantly atmospheric or vacuum residues, the concentration of 3 to 7-ringed PAHs will be around 6-8%, whereas if larger quantities of cracked components are used, the PAH level may approach 20% (IARC 1989). As an example, concentrations of 11 PAHs including phenanthrene (482 mg l⁻¹), 2-methylphenanthrene (828 mg l⁻¹), fluoranthene (240 mg l⁻¹), chrysene (196 mg l⁻¹) and benz(a)anthracene (90 mg l⁻¹) have been reported in Fuel Oil No 6 (cited in IARC 1989). For a detailed review of the relative environmental hazards posed by PAHs see the corresponding WRc report for these compounds (Grimwood 1996).

Residual fuel oils may also contain additives to improve combustion. These are mostly based on oil-soluble compounds (e.g. naphthenates) of calcium, cerium, iron and manganese. Concentrations vary with fuel type, but typically range from 50 to 300 mg metal ion l⁻¹ (IARC 1989).

A4.2 Uses

In general, residual fuel oils are used by electric utilities, the maritime industry, industrial and commercial plants, and in the petroleum industry in the production of process steam, space and water heating. Electric power generation is the most important use, with 39% of total US domestic consumption used for this purpose in 1983 (IARC 1989).

A4.2.1 Fuel Oil No 4

Fuel Oil No 4 is intended for use in burners equipped with devices that atomize oils of higher viscosity than domestic burners can handle. Its lower viscosity than that of Fuel Oil No's 5 and 6 allows it to be pumped and atomized at relatively low temperatures. Consequently, it requires no preheating before use, in all but the coldest weather (IARC 1989).

In addition, Fuel Oil No 4 is essentially similar in properties to Diesel Fuel No 4. The later is a distillate marine fuel which can also be used in trains, river barges and for stationary engines in continuous high load service (IARC 1989).

A4.2.2 Fuel Oil No 5

Fuel Oil No 5 is a residual fuel of intermediate viscosity for burners capable of handling fuel more viscous than Fuel Oil No 4. Some preheating may be necessary in some types of equipment, especially in colder climates (IARC 1989).

A4.2.3 Fuel Oil No 6

Fuel Oil No 6, sometimes referred to as "Bunker Fuel" or "Bunker C", is a high viscosity oil used mostly as a boiler fuel in commercial and industrial heating. It requires pre-heating in storage tanks to permit pumping and additional preheating at the burner to permit atomizing. The extra equipment and maintenance required to handle this fuel usually precludes its use in smaller installations (IARC 1989).

A4.3 Production/consumption

Figures specifically relating to each residual fuel oil do not appear to be available. However, IARC (1989) have reported respective production and consumption figures (1985) for total residual oil for the 24 countries of the OECD, of 233 256 and 103 862 thousand tonnes. This contrasts with corresponding production/consumption figures of 418 508 / 199 351 and 444 033 / 228 964 thousand tonnes in 1980 and 1975, respectively. The figures suggest a general decrease in the manufacture and use of these products. A corresponding figure of 13 204 thousand tonnes has been reported for UK production in 1992 (Betton 1994), equal to 15.5% of all products produced from crude oil.

A4.4 Routes of entry to the aquatic environment

The main route of residual fuel oil entry to the aquatic environment is likely to be as a result of accidental spillage of distillate marine fuel and heating oil during storage, transport and use.

A4.5 Reported environmental concentrations

The only available data specifically relating to measured concentrations of residual fuel oils in surface waters, relates to concentrations of 0.01-0.02 mg l⁻¹ detected in the Gulf of Bothnia two weeks after a 200 tonne spill of "heavy fuel oil" from a grounded tanker (Vainio *et al* 1987). Concentrations had reduced to background levels around 1 month after the spill. The total hydrocarbon content in sediments of the Gulf varied from 1 to 130 mg kg⁻¹, suggesting that the sediments were not greatly impacted in this case.

The following incidents give an indication of the magnitude of spillages that can occur. In 1970, 1980 and 1983, 1.75 million litres, 8100 tonnes and 284 000 litres of “Bunker C” (Fuel Oil No 6) were spilt in Canada, France and the US, respectively, following incidents involving grounded and wrecked tankers. Similarly, in 1977 more than 1,000 tonnes of Fuel Oil No 5 were spilt in Sweden following the grounding of a tanker (cited in IARC 1989).

A4.6 Fate, behaviour and persistence in the aquatic environment

On entering aquatic ecosystems, residual fuel oils will break into small masses and will not spread as rapidly as less viscous petroleum products. Loss of the lower molecular weight components due to volatility and dissolution will increase the density of the remaining oil, causing it to sink. This heavy fraction will assume a tar-like consistency and stick to exposed substrates or become adsorbed to particulate matter. Resuspension of these residues could lead to contaminant spread and continued impact on benthic organisms (D. Short, CONCAWE, Pers. Comm. 1996).

Sedimentation has been shown to be an important removal mechanism of residual fuel oil from the water column. During the second week following a spill of Fuel Oil No 5 from a tanker in 1977, 0.7% of sediment collected at the site (detritus and clay particles) was contaminated with the oil. In all, 30-60 tonnes of oil remaining after the clean-up operation was transported to the bottom by sedimentation (D. Short, CONCAWE, Pers. Comm. 1996).

The composition of residual fuel oil will change dramatically during weathering processes. Initially, a rapid loss of the low molecular weight compounds by volatilisation, dissolution and biodegradation will occur, resulting in almost complete removal of *n*-alkanes up to C₁₇ in the first year following a spill. Removal of the more persistent pristane and phytane will be less rapid, but these compounds should be biodegraded within a few years. The non-*n*-alkane components will be the most resistant to biodegradation and could persist for many years. In 28-day laboratory tests with crude and refined oils, “Bunker C” (Fuel Oil No 6) was the least biodegraded (11% compared to 51-82% for crude) due to its higher proportion of high molecular weight aromatics (D. Short, CONCAWE, Pers. Comm. 1996).

A4.7 Toxicity to aquatic organisms

Interpretation of the available toxicity dataset for residual fuel oils is complicated by the variety of test methodologies used in its generation. Most data are derived from studies in which the Water Soluble Fraction (WSF) was used, with toxicity measured either as mg l⁻¹ of soluble hydrocarbons, or as the percentage dilution of the stock WSF. In addition data are also available from studies in which oil-in-water (OWD) dispersions were tested. However, the WSF method assumes that organisms are exposed only to truly dissolved hydrocarbons and does not account for exposure to undissolved, dispersed oil droplets. Moreover, it is not possible to accurately correlate concentrations of hydrocarbons in the WSF with the amount of product that must be added to the exposure medium to produce the effect of concern. In addition, the use of OWDs is not considered to be a consistent method for determining intrinsic toxicity of whole petroleum products. Therefore, the most appropriate procedure for ecotoxicity testing of complex hydrocarbon mixtures is the Water Accommodated Fraction (WAF) method, whereby effect concentrations are expressed both in terms of the water soluble fraction plus hydrocarbons present as dispersed droplets. Moreover WAF results are expressed as consistent “loading rates” (i.e. amount of product added to the exposure medium

causing an effect e.g. LL50) which makes determination of the intrinsic toxicity of a whole petroleum product more reliable. (CONCAWE 1994). These issues are discussed more fully in Section 6.1 of the main report.

Therefore, observed differences in toxicity of different residual fuel oils (i.e. No's, 4, 5 and 6) and between different species, may be as much due to differing test methodologies employed, as to inherent differences in product toxicity and species sensitivity. Moreover, a further complication is that the toxicity of residual fuel oils is also dependent on the quantity and type of lower molecular weight blending stock used in their preparation. It is therefore very difficult to characterise the toxicity of these products to any great precision.

Nevertheless, The available data reported as WSFs (no available WAF data) indicate that residual fuel oils are of moderately high acute toxicity to sensitive crustaceans and fish, with effect concentrations ranging from 0.9-3.1 mg l⁻¹ (see Table A4.2). In the absence of a blending stock, toxicity appears to be lower. For example, the 48 hour EC50 for the water flea (*Daphnia magna*) following exposure to Fuel Oil No 6 containing no bending stock, was greater than the 100% WSF (i.e. undiluted WSF). However, no details are available concerning the concentration of different hydrocarbons in the WSF (mg l⁻¹). The limited data available suggest that algae and macrophytes are of lower sensitivity than crustaceans and fish. An EL50 (loading rate) of 160 mg l⁻¹ (OWD) has been reported for *Skeletonema costatum* exposed to Fuel Oil No 6, while a 100% WSF had no effect on most species of duckweed (*Lemna* spp.) tested.

Table A4.2 Aquatic toxicity of residual fuel oils

SPECIES	EXPOSURE DURATION	EFFECT	CONC (mg l ⁻¹)	COMMENTS	REF
Algae					
<i>Skeletonema costatum</i> (Diatom)	-	EL50 (biomass)	160.0	OWD, Fuel Oil No 6. Saltwater species	1
<i>Selenastrum capricornutum</i>	16 hours	No growth inhibition Growth stimulation	100% 0.1%	WSF, Fuel Oil No 6, without blending stock	3
Macrophytes					
<i>Lemna minor</i> (Duckweed)	8 days	18% growth reduction	50-100%	WSF, Fuel Oil No 6	2
<i>Lemna gibba</i> , <i>L. perpusilla</i> (Duckweed)	8 days	No effect on growth	100%	WSF, Fuel Oil No 6	2
Crustaceans					
<i>Mysidopsis almya</i> (Mysid shrimp)	48 hours	LC50	0.9	WSF, "Bunker C". Saltwater species	4
<i>Penaeus aztecus</i> (Brown shrimp)	96 hours	LC50	1.9	WSF, "Bunker C".	4

SPECIES	EXPOSURE DURATION	EFFECT	CONC (mg l ⁻¹)	COMMENTS	REF
shrimp)				Saltwater species	
<i>Daphnia magna</i> (Water flea)	48 hours	EC50	>100%	WSF, Fuel Oil No 6, without blending stock	3
Fish					
<i>Fundulus similis</i> (Longnose killifish)	96 hours	LC50	1.7	WSF, "Bunker C"	4
<i>Cyprinodon variegatus</i> (Sheepshead minnow)	96 hours	LC50	3.1	WSF, "Bunker C". Saltwater species	4
<i>Brachydanio rerio</i> (Zebra fish)	96 hours	LL50	48.0	Method not clear. Fuel Oil No 6 ("Carbon Black Oil")	5
<i>Fundulus diaphanus</i> (Banded killifish)	96 hours	LC50	21.0	Fuel Oil No 4. No details of methodology	6
<i>Morone saxatilis</i> (Striped bass)	96 hours	LC50	25.0	Fuel Oil No 4. No details of methodology	6

Notes to Table A3.2:

EL50 Median Effect Loading Rate

LL50 Median Lethal Loading Rate

NOEL No-Observed Effect Loading Rate

OWD Oil in Water Dispersion. In terms of mg of oil added to exposure medium (analogous to loading rate) (See Section 5.1)

WSF Water Soluble Fraction. In terms of mg of total dissolved hydrocarbons in the WSF following mixing and separation of oil in the exposure medium (See Section 6.1)

References

- 1 Hollister et al (1980)
- 2 King and Coley (1984)
- 3 Giddings et al (1980)
- 4 Anderson et al (1974b)
- 5 DSM Kunststoffen B. V. (1989)
- 6 Rehwoldt *et al* (1974)

A4.8 Bioaccumulation potential

Interpretation of bioaccumulation data of petroleum products in fish also presents some difficulties since each constituent compound bioaccumulates to the extent determined by its own physico-chemical properties and so each component ideally needs to be measured independently (CONCAWE 1992, see Section 5.1.2). Available data concerning the bioaccumulation of residual fuel oils are extremely limited. A 20-fold increase has been reported in the gills, liver and kidney of rainbow trout (*Oncorhynchus mykiss*) exposed to chlorine-labelled Bunker C (D. Short, CONCAWE, Pers. Comm. 1996). Since a linear

increase in biota with increasing exposure concentrations was only observed in muscle tissue, the authors concluded that the kidney and liver metabolised the accumulated hydrocarbons to some extent.

Bioaccumulation has also been recorded in the field after accidental oil spills. For instance, hydrocarbon concentrations in mussels (*Mytilus edulis*) rapidly increased (over 60 days) following the grounding of a tanker in 1977. One year after the spill tissue concentrations were still elevated compared to background concentrations. A similar uptake pattern was observed in the deposit-feeding clam (*Macoma balthica*), although, unlike the mussel, little depuration was observed. The authors attributed this to continuous exposure of the organism to oil, as a result of resuspension of petroleum-bearing particulates from benthic sediments (D. Short, CONCAWE, Pers. Comm. 1996). Anderson *et al* (1974b) also found that clams readily accumulate residual fuel oils. The authors found that naphthalene, methylnaphthalene and dimethylnaphthalene were the hydrocarbons accumulated to the greatest extent. Following removal to clean seawater, depuration of these compounds took from 10 to 52 days

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B1 DESCRIPTION

Lubricating oils are substances intended to reduce friction between surfaces in relative motion. They may also serve other, secondary purposes, such as heat transfer liquids, in metal processing, for protection against corrosion and in medicinal/food uses. Since the 1930s, nearly all the worlds lubricating oils have been produced by refining distillate or residual fractions obtained directly from petroleum crude oils (IARC 1984). Moreover, since this review is chiefly concerned with prioritising different *petroleum* products in terms of environmental hazard/risk, little attention has been given to the few synthetic lubricating oils that have recently appeared on the market. Examples of *synthetic* oils used in the water industry include silicones, polyglycols, glycerides and polyalphaolefins (Hegarty *et al* 1995). In addition, some lubricating oils are based on natural oils (triglyceride esters) such as rapeseed, sunflower and palm oil (Betton 1994).

In the following discussion of lubricating oils, the term “lubricant *base* oils” is used to refer to vacuum distillates of a crude oil refinery which have undergone some finishing process to produce a specific base oil, whereas a “lubricating oil” is considered to be a commercial end product marketed for lubricating purposes, which may or may not contain performance-enhancing additives. This review chiefly concentrates on lubricant *base* oils, as environmental data on commercial formulations are generally only available from the manufacturers of such products, who are usually reluctant to disseminate this data in full detail.

B1.1 Lubricant base oils

B1.1.1 Production process and base oil classification

Following atmospheric distillation to fractionate crude oil into various fuel components (see Appendix A for appropriate profiles), the vacuum distillation unit of an oil refinery is fed with the atmospheric residuum. This residuum is then further fractionated into distillates of progressively increasing viscosity, carbon number and boiling point range. The principal lubricant fractions, distillates and the vacuum residuum are then further processed in modern lubricant refineries to produce a range of base oils. This is shown clearly in Figure 2.1 in Section 2 of this report.

It is the severity of the final refinery process that is used to classify lubricating base oils. The categories defined by IARC (1984) are shown in Table B1.2. The classification is based on increasing severity of processing or refinement. Furthermore, within each class a range of additional treatment severities is possible. Commercial lubricating oils in Class 7 comprise of formulations of various base oils from the previous categories, together with chemical additives (exact composition usually not known - see Section B1.2).

Table B1.2 IARC (1984) categories of petroleum derived lubricating base oils

CATEGORY	DESCRIPTION/REFINERY PROCESS	FINISHING STEPS
Class 1	Vacuum distillates	Subsequent finishing processes include caustic neutralisation, dewaxing, clay treatment and/or mild hydrotreatment. Not acid treated or solvent extracted
Class 2	Acid-treated soils	Subsequent finishing processes include caustic neutralisation, dewaxing, clay treatment and/or mild hydrotreatment. Not solvent extracted
Class 3	Solvent-refined oils (raffinates)	Subsequent finishing processes include dewaxing, clay treatment and/or mild hydrotreatment
Class 4	Hydrotreated oils	
Class 5	White oils suitable medicinal/food use	
Class 6	Aromatic oils <ul style="list-style-type: none">- 6.1. Solvent extracts- 6.2. Catalytically cracked oils	
Class 7	Miscellaneous materials <ul style="list-style-type: none">- 7.1. Formulated oils- 7.2. Used oils	
Class 8	Petroleum derived materials not otherwise categorised (i.e. not sufficiently described to allow assignment to other classes)	

B1.1.2 Chemical composition

The chemical composition of a lubricating base oil depends on both the parent crude from which it is derived and the processes used in refining the base oil. With simple refining techniques, the composition of the finished base oil reflects that of the parent crude. However, with more severe refining processes, variations in the composition of the base oil are more to do with the refinery process than due to variations in the original crude.

Lubricant base oils are complex mixtures of straight and branched-chain paraffinic, naphthenic (cycloparaffin) and aromatic hydrocarbons having carbon numbers of 15 or more and boiling points in the range of around 300-600 °C. Heavier lubricant base oils obtained from residual fractions may have components that boil as high as 815 °C. The proportions of the different hydrocarbon species present are responsible for the different characteristics of the base oils. The higher the molecular weight of its hydrocarbon constituents, the more viscous is the oil (IARC 1984).

A lubricant refinery stream may be described as generally paraffinic or generally naphthenic, as determined by the source of the crude oil. Paraffinic crude oils are characterized by high wax content, high natural viscosity index (low rate of change in viscosity with temperature) and relatively low aromatic hydrocarbon content. Naphthenic crudes are normally low in wax and relatively high in cycloparaffins and aromatic hydrocarbons (IARC 1984).

Impurities in lubricant base oils

All crude oils contain polycyclic aromatic hydrocarbons (PAHs), with compounds and quantities dependent on the source of the crude. However, the PAHs present in finished lubricant base oils are determined mainly by the refinery processes employed in their production. Mild processing such as acid/clay treatment slightly reduces the total aromatic hydrocarbon content but does not significantly reduce the amount of PAHs. Mild hydroprocessing, on the other hand, reduces the PAH content but has little effect on the total aromatic content. Solvent extraction, or severe hydroprocessing reduces both PAH and total aromatic content substantially. Sufficiently severe treatment with fuming sulphuric acid (oleum) can remove aromatics including PAHs almost entirely, for example, to produce white oils of medicinal quality (IARC 1984).

A wide range of PAHs have been identified in unused engine lubricating oils. Grimmer *et al* (1981, cited in IARC 1984) reported concentrations of up to 11.9, 9.4, 6.5 and 0.4 mg kg⁻¹ for benzo(b)naphtho[2,1-*d*]thiophene, chrysene, pyrene and benzo(e)pyrene (the four most frequently detected, in this order), respectively. Other less frequently detected compounds (with highest reported concentrations as mg kg⁻¹) include benzofluranthenes (0.23), fluoranthene (2.8), benzo(a)pyrene (0.27), perylene (0.22), benzo(g,h,i)perylene (0.14), coronene (0.02), anthracene (0.03) and indeno(1,2,3-*cd*)pyrene (0.02).

There is also strong evidence to suggest that the PAH content of lubricating oils may increase during use (Grimmer 1983, cited in IARC 1984). The extent of the increase appears to depend on the type of application; up to 10-fold for cutting oils and diesel-engine oils, but around 100-fold or more for gasoline-engine oils and heat-treating oils. Much of the PAH increase in engine oils is as a result of gasoline combustion. Non-engine lubricating oils such as hydraulic and gear oils, would not be expected to undergo any significant increase in PAH content during use because of the limited increases in temperature to which they are subjected (CONCAWE 1983, cited in IARC 1984). A similar increase in the aromatic content of used crankcase oils has been noted by Mahaney (1994).

The consequences of PAH discharge to aquatic ecosystems and priorities based on relative hazards/risks, are discussed in detail in the corresponding WRc report for these compounds (Grimwood 1996).

It is also worth noting that used gasoline-engine oils can contain up to 1% lead, as a result of lead additives in gasoline. Similarly, used transformer oils can contain various levels of polychlorinated biphenyls (PCBs), owing to the previous use of these compounds for this purpose (IARC 1984).

B1.2 Lubricating oils (commercial products)

Lubricant refinery streams produce the base oils which form the basis of commercial lubricating oils. Depending on the specific application, one or more additives may be incorporated into the chosen refinery stream(s) in amounts ranging from a few mg kg⁻¹ to 20% by volume, although typically individual additives are present at less than 2%. Automotive crankcase lubricants are by far the largest market for additives, but they are also widely used in many industrial lubricants to impart or enhance the technical characteristics required for many special applications.

Additives are usually proprietary materials and not necessarily well defined chemical substances. Examples of additive components include viscosity index improvers, pour-point depressants, tackiness agents, anti-foam additives, emulsifiers, friction modifiers, antioxidants, anti-rust additives, metal deactivators, antiwear/extreme pressure additives, detergents/dispersants and biocides (IARC 1984).

Since, environmental data on commercial lubricating formulations are generally only available from the manufacturers of such products, who are usually reluctant to disseminate this information in full detail, the amount of data included in this review on commercial oils (inclusive of additives) is limited.

B2 USES

The lubricant base oils described above are used in a broad range of products. The principal base oils are produced predominantly from paraffinic crudes and used for lubrication of internal combustion engines and a wide variety of industrial, non-engine machinery e.g. gears, bearings and pumps. Refined naphthenic base oils are used to a lesser degree and for specific applications in which their low-temperature properties and other characteristics, such as their good solubility for additives, are required (IARC 1984).

Since most of the concepts and technology utilised in formulating products are proprietary to manufacturers, these matters can only be discussed in general terms. Table B2.1 (CONCAWE 1983, reproduced from IARC 1984) addresses the issue from the standpoint of different applications of lubricating oils in terms of general composition (N.B. Table B1.2 also includes greases, which are lubricating oils thickened with metallic soaps or certain organophilic clays). It gives a general introduction of how the main types of lubricants for different applications fall into different compositional groups. The table lists for each application, the compositional groups mainly used, sometimes used and only occasionally used. In addition, lubricant oils are divided into two broad groups: those that are *highly refined* and those that have only undergone, at best, very *limited refining*. *Highly refined* oils are likely to have been severely hydrotreated and/or severely solvent refined (extracted) or oleum-treated. Those oils described as having undergone *limited refining* are those that have been subjected only to sulphuric acid/clay treatment, mild solvent refining (extraction) or mild hydrotreatment.

Table B2.1 Classification of lubricant use by compositional group^a (CONCAWE 1983, reproduced from IARC 1984)

B3 PRODUCTION/CONSUMPTION

Total world production and consumption figures in 1980 for lubricant base oils was reported to be 26 100 and 23 800 thousand tonnes, respectively (Stewart and Helm 1980, cited in IARC 1984). Corresponding figures for Western Europe were 6500 and 6000 thousand tonnes. In addition, a figure of 973 thousand tonnes has been reported for UK production in 1992 (Betton 1994), equal to 1% of all products produced from crude oil.

Total US sales of products derived from lubricant oil refinery streams amounted to 8650 thousand tonnes in 1981 and consisted of the following (in thousands of tonnes): lubricating oils (7360), waxes (700), aromatic oils (370) and greases (210). Over 50% of all lubricating oils sold went into automotive and engine oils (Wills 1980, cited in IARC 1984).

B4 ROUTES OF ENTRY TO THE AQUATIC ENVIRONMENT

The main route of entry for large quantities of lubricating oils to the aquatic environment is likely to be as a result of accidental/intentional spillage during storage, transport and use. Some examples include, road run-off of used engine oils (used crank case oil is the main source of petroleum hydrocarbons, particularly PAHs, in road run-off; Maltby *et al* 1995), unlawful disposal of used engine oils directly into surface waters and surface water drains, discharge of used/unused oils from river boats and barges and release of lubricating oils from machinery (e.g. gears and pumps) that comes into close contact with surface waters (e.g. abstraction points, weirs, locks, etc).

B5 REPORTED ENVIRONMENTAL CONCENTRATIONS

Hydraulic oil was detected in samples of industrial cooling water during 1971, 1973 and 1974 in the UK (Nicholson and Taylor 1975, cited in IARC 1984). Infrared analysis showed levels of soluble and total oil to be 20-46 and 37-56 mg l⁻¹, respectively. This appears to be the only available published data relating to the discharge of lubricating oils to surface waters. However, Maltby *et al* (1995) have reported total hydrocarbon concentrations of 1014-1806 mg kg⁻¹ in sediments of small northern England streams receiving motor-way run-off chiefly consisting of used crank case oil. These values are expressed in terms of lubricant *base* oil-equivalents.

B6 FATE, BEHAVIOUR AND PERSISTENCE IN THE AQUATIC ENVIRONMENT

Since lubricant base oils and commercial formulations consist of hydrocarbon molecules of a similar size to those in the heavy fuel oils (i.e. around C₁₅ to C₅₀ - see Section A4), on entering aquatic ecosystems, the main removal route of lubricating oils will be adsorption onto suspended solids and sediments, followed by very slow biodegradation. The minimal loss of the small percentage of compounds with a relatively lower molecular weight by volatilisation, will increase the density of the remaining oil, causing it to sink. (D. Short, CONCAWE, Pers. Comm. 1996).

Lubricating oils consist of a greater proportion of high molecular mass compared to low molecular mass compounds. This leads to a high resistance to complete biodegradation (i.e. to carbon dioxide, water and inorganic salts). This limited capacity for biodegradation under natural conditions has been shown by Xie *et al* (1995). In this study the authors reported biodegradation rates of only 15-23% of 4 lubricating oils with different compositional qualities in terms of molecular weights and aromatic content, following 67 days incubation with Great Lake water containing just indigenous microbial populations. The slow rates of biodegradation were attributed to low initial microbial numbers ($<10^4$ cells ml⁻¹), the restricted ability of the natural population to utilise the lubricant hydrocarbons as a sole carbon source and the slow adaptation of the microbial population as shown by the reduction in cell numbers over the 67 days.

In a study of the biodegradability of a range of base oils, CONCAWE also found that lubricating oils are only completely biodegraded very slowly as shown in tests for *ultimate* biodegradability (D. Short, CONCAWE, Pers. Comm. 1996). In 28 day Sturm tests, the highest value reported was 22% complete biodegradation (i.e. to CO₂) for a 20 mg l⁻¹ concentration of a solvent-refined paraffinic distillate. Biodegradation decreased with increasing viscosity of the lubricant base stock, such that the lowest value reported in the Sturm test was just 2% for a solvent refined residual oil.

Similar figures for complete biodegradation have been reported in other studies. For instance Battersby *et al* (1992) reported 6% and 21% biodegradation of solvent de-waxed residual oil and solvent de-waxed heavy paraffinic oil, respectively, in a 28-day modified Sturm test (OECD 301B).

The above “ready” biodegradability studies measure the potential for complete (or *ultimate*) biodegradation (i.e. conversion to CO₂, water, inorganic salts and new biomass). Currently, the only recognised method for testing the biodegradability of lubricating oils is the CEC L-33-A93 test, originally developed to measure the biodegradability of two-stroke outboard engine lubricants (although it has become the *de facto* method for assessing the biodegradability of other petroleum products). However, the CEC test really only gives a measure of “primary” biodegradation (i.e. *inherent* biodegradability). In other words, it only detects the breakdown of the parent compound to its metabolites, rather than complete mineralisation to CO₂. Therefore, results of CEC tests for biodegradability of lubricating oils tend to be higher and so may give a falsely optimistic picture of their biodegradation under field conditions (Battersby 1995). Indeed, corresponding 21 day biodegradation figures obtained in the CEC test for the base lubricants discussed in the above CONCAWE study, were 63% and 45%, respectively (D. Short, CONCAWE, Pers. Comm. 1996), while corresponding CEC test values for the two lubricant oils tested by Battersby *et al* (1992, see above) were 28% and 45%, respectively.

White mineral oils appear to be particularly resistant to biodegradation, with 0 and 10% removal reported for 20 mg l⁻¹ in the 28 day Sturm test for “ultimate” biodegradability and the 21-day CEC test for “primary” biodegradability, respectively (Battersby *et al* 1992).

Biodegradability of synthetic base lubricants

It is worth pointing out that synthetic base oils appear to be more susceptible to microbial degradation than petroleum-derived base oils. For example, in the CEC tests for primary biodegradability conducted by Carpenter (1995), synthetic polyalphaolefins of relatively low viscosity were biodegraded by 60-70% over 21 days, whereas equally viscous mineral oils were only biodegraded by around 20-30% in this test. However, biodegradation of the synthetic base oil in the CEC test dropped to between 5 and 20% as viscosity increased. Biodegradation of all the synthetic polyalphaolefins tested appeared to reach a maximum peak (plateau) at around day 20-30, with little additional biodegradation beyond this point, as measured in extended tests (120 days).

B6 TOXICITY TO AQUATIC ORGANISMS

Interpretation of the available toxicity dataset for lubricant base oils is complicated by the variety of test methodologies used in its generation. Some data are derived from studies in which the Water Soluble Fraction (WSF) was used, with toxicity measured either as mg l^{-1} of soluble hydrocarbons, or as the percentage dilution of the stock WSF. In addition data are also available from studies in which oil-in-water (OWD) dispersions were tested. However, the WSF method assumes that organisms are exposed only to truly dissolved hydrocarbons and does not account for exposure to undissolved, dispersed oil droplets. Moreover, it is not possible to accurately correlate concentrations of hydrocarbons in the WSF with the amount of product that must be added to the exposure medium to produce the effect of concern. In addition, the use of OWDs is not considered to be a consistent method for determining intrinsic toxicity of whole petroleum products. Therefore, the most appropriate procedure for ecotoxicity testing of complex hydrocarbon mixtures is the Water Accommodated Fraction (WAF) method, whereby effect concentrations are expressed both in terms of the water soluble fraction plus hydrocarbons present as dispersed droplets. Moreover WAF results are expressed as consistent “loading rates” (i.e. amount of product added to the exposure medium causing an effect e.g. LL50) which makes determination of the intrinsic toxicity of a whole petroleum product more reliable. (CONCAWE 1994). These issues are discussed more fully in Section 6.1 of the main report.

B6.1 Base oils

The available data indicate that all lubricant *base* oils are not acutely toxic to aquatic organisms (see Table B6.1). LL50 values (“loading rates”) for rainbow trout (*O. mykiss*) range from >1000 to $>10\ 000\ \text{mg l}^{-1}$ (OWD), following 96 hours exposure (D. Short, CONCAWE, Pers. Comm. 1996). In addition, 48-96 hour EL50s of $>100\ 000$ and $>10\ 000\ \text{mg l}^{-1}$ (“loading rates”) have been reported for the water flea (*D. magna*) and freshwater shrimp (*Gammarus pulex*), following exposure to WSFs and WAFs, respectively (D. Short, CONCAWE, Pers. Comm. 1996).

Mahaney (1994) has reported that used crank-case oil concentrations as low as $10\text{-}100\ \text{mg l}^{-1}$ caused growth reduction in tadpoles of the tree frog, *Hyla cinera* 13 days after hatching, although no effects were observed on hatching success or survival. These results still indicate low chronic toxicity. In addition, the relevance of these results to amphibian species indigenous to the UK is uncertain. Moreover, the higher toxicity in this study can probably be

attributed to the greatly increased PAH levels in used automotive lubricating oil relative to that in virgin oils.

Table B6.1 Aquatic toxicity of lubricant base oils

SPECIES	EXPOSURE DURATION	EFFECT	CONC (mg l ⁻¹)	COMMENTS	REF
Crustaceans					
<i>Daphnia magna</i> (Water flea)	48 hours	EL50	>100,000	WSF, Technical white oil and paraffinic base oil	1
<i>Daphnia magna</i> (Water flea)	48 hours	EL50	>10,000	WAF, Solvent refined light naphthenic distillate	1
<i>Gammarus pulex</i> (Freshwater shrimp)	48 hours	EL50	>10,000	Ditto	1
Fish					
<i>Oncorhynchus mykiss</i> (Rainbow trout)	96 hours	LL50	>1,000	OWD, Solvent refined paraffinic distillates, Solvent refined hydrocracked distillates and Solvent/non-solvent refined residual oil	1
<i>Oncorhynchus mykiss</i> (Rainbow trout)	96 hours	LL50	>10,000	OWD, Technical white oil and paraffinic base oil	1
<i>Oncorhynchus mykiss</i> (Rainbow trout)	96 hours	LL50	>2,000	OWD, Proprietary lithium-complexed grease (no additives)	1
<i>Oncorhynchus mykiss</i> (Rainbow trout)	96 hours	LL50	>5,000	OWD, Paraffinic neutral (various viscosities) and paraffinic bright	1

Notes to Table A3.2:

EL50 Median Effect Loading Rate

LL50 Median Lethal Loading Rate

OWD Oil in Water Dispersion. In terms of mg of oil added to exposure medium (analogous to loading rate) (See Section 5.1)

WAF Water Accommodated Fraction. In terms of mg of oil in the WSF (see below) plus that in the form of undissolved, dispersed droplets following mixing and separation in the exposure medium (See Section 6.1)

WSF Water Soluble Fraction. In terms of mg of total dissolved hydrocarbons in the WSF following mixing and separation of oil in the exposure medium (See Section 6.1)

References

1 D. Short, CONCAWE, Pers. Comm. 1996).

B6.2 Commercial lubricating oils

Some very general toxicity data are available in the public domain for commercial formulations inclusive of additives (Girling *et al* 1993). The results of these tests suggest that commercial formulations may be more toxic than the base oils. It is conceivable that the presence of additives in the commercial products is responsible for the increased toxicity.

Following exposure of the water flea, *D. magna* and rainbow trout (*O. mykiss*) to eleven commercial lubricant products in WAF tests (see Table B6.2), eight of the products were not acutely toxic, with observed L(E)50s (“loading rates”) of >10 000 mg l⁻¹. The three other products were of higher toxicity to rainbow trout, but still low, with LL50s ranging from 100-10 000 mg l⁻¹. *D. magna* was somewhat more sensitive to two of these latter products, with EL50s of 10-100 and <10 mg l⁻¹, indicating moderate acute toxicity. In this study the alga, *Selenastrum capricornutum*, appeared to be more sensitive than the crustacean and the fish following exposure to all except one of the lubricants. However, even for this sensitive organism, eight of the products were still of low acute toxicity. The results of these studies are shown more clearly in Figure B6.1.

Table B6.2 Commercial lubricants subjected to testing

1	Low viscosity cutting oil
2	Lubricating oil for needle mechanisms
3	Medium viscosity turbine lubricant
4	“Universal” oil for diesel and gasoline vehicle engines
5	Two-stroke outboard motor oil
6	Synthetic lubricant based on vegetable oil
7	Diesel engine lubricant
8	Gear oil
9	Extreme pressure gear oil
10	Heavy duty gear oil
11	Synthetic gear oil

Figure B6.1 Toxicity of eleven lubricants to three freshwater species (from Girling *et al* 1993)

Toxicity of Additives in commercial formulations

While it is not in the remit of this review to assess the environmental hazards of additive compounds themselves, it is worth pointing out that the Technical Committee of Petroleum Manufacturers in Europe (ATC) and the Chemical Manufacturers Association (CMA) in the US, have concluded that the majority of additive compounds are not acutely toxic to aquatic organisms as tested by the Water Accommodated Fraction (WAF) method (Linnet *et al* 1996). Only the zinc alkyl and alkaryl dithiophosphates exhibited high acute toxicity to some species. However, the authors concluded that given the low solubility of these compounds and low potential for exposure, the risk of harm to aquatic organisms is very low, even for those exhibiting acute toxicity. Nevertheless, highly toxic additives may exacerbate the effects of lubricating oils on exposed organisms.

B7 BIOACCUMULATION POTENTIAL

Interpretation of bioaccumulation data of petroleum products in fish also presents some difficulties since each constituent compound bioaccumulates to the extent determined by its own physico-chemical properties and so each component ideally needs to be measured independently (CONCAWE 1992, see Section 6.1.2). The typically high log Kow values of hydrocarbons in lubricating oils (3.9->6) indicate that they may have the potential to bioaccumulate, although the low BCFs reported for light and heavy fuel oils (only around 20, see Sections A3 and A4) suggest that the hydrocarbon constituents of these complex mixtures are unlikely to be bioaccumulated to high levels. This is especially true for the lubricating oils, which tend to have a greater proportion of molecules with a higher molecular size, for which steric hindrance/reduced bioavailability may limit bioaccumulation. However, there are no available data to confirm this.

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