MANAGING WATER QUALITY IN RELATION TO THE PETROCHEMICAL INDUSTRY

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ABSTRACT

The paper reviews the impact of petrochemicals on the aquatic environment from the viewpoint of the water manager. It concentrates on the effects of refinery effluents. Oil products can disrupt the ecology of environmental waters and render the management of sewerage and sewage treatment systems difficult. Water management can utilise different approaches to the avoidance of deleterious effects and that favoured by the UK involves the use of quality objectives. These can be used to calculate acceptable effluent quality limits. Continued achievement of the objectives must rely on satisfactory monitoring and analytical methods. With the international nature of oil pollution, international analytical methods are being introduced.

KEYWORDS

Water Quality, petrochemicals, effluent limits, monitoring, analysis.

INTRODUCTION

The growth of modern society has relied substantially on the production of petrochemicals from crude mineral oil. It can justly be said that many materials are derived in this way, but the subject of this paper will be the impact of petroleum on water and in particular refinery effluents.

The petroleum industry has become world wide and very substantial. For instance, the UK government is selling 31.5% of the shares in British Petroleum and these are considered to be worth £7.5B. The industry is multi-national and it is, therefore, legitimate to consider that the same pollution control philosophies are applicable in different continents and countries.

Of course local environmental circumstances and economies may play roles in determining the most appropriate criteria in practice.

In addition to the refinery effluents there are other aspects of petroleum products which require attention. There is the transport and unloading of petroleum oils and it is well known that bulk conveyance can cause catastrophic water pollution incidents. Spectacular major accidents with ship tankers have been publicised, but there are also many minor accidents involving smaller ships. Another source of concern is the routing of road tankers; if these crash into vulnerable environmental waters and release their oil contents the resulting effect can be serious locally. Such hazards must be taken into account, for instance, when the vulnerability of sources of fresh water used for drinking purposes is assessed. It is bad practice to locate such intakes downstream of major road bridges.
The use of petroleum products can also give rise to potential pollution, particularly when they are truly used rather than consumed. The disposal of spent oil, such as from cars, has been a source of concern for many years in the UK. For instance, in 1974 it was estimated that do-it-yourself motorists in the UK disposed of 65,800 m$^3$ of used car oil every year of which 5,300 m$^3$ is discharged into public sewers (Matthews, 1986). No current figures are available but it is undoubted that they have risen. Some municipal authorities provide central collection facilities for domestic oil which is then removed by reclamation companies. The practice is not widespread but growing. However, the European Community has a Directive requiring action by Member States for the disposal of waste oil (European Community, 1975).

The oil may be tipped down surface water sewers from whence it is often discharged direct to rivers. Equally, highway drainage may be contaminated with oil. For 1986/7 Anglian Water (a water authority responsible for water cycle management in Eastern England) reported that 502 out of 1,468 principal pollution incidents affecting freshwaters related to oil and related products as opposed to 14 out of 39 affecting saline waters.

Of course crude oil recovery itself is a serious potential source of pollution, particularly now that marine platforms are becoming common-place. There have been "blow-outs" in the European North Sea-Ekofisk and in the Gulf of Mexico, for instance, and these cause direct in-situ pollution.

Atmospheric pollution and natural seepage may also contribute to the presence of petrochemicals in water bodies. The relative contributions of these sources have been assessed as a "worst case" for the European North Sea. The actual values are likely to be lower, the data, in being estimates are considered to be deficient. Data are given in Table 1 (McIntyre 1987).

<table>
<thead>
<tr>
<th>Source</th>
<th>Load. $10^5$ tonnes</th>
</tr>
</thead>
<tbody>
<tr>
<td>Shipping</td>
<td>100</td>
</tr>
<tr>
<td>Rivers</td>
<td>80</td>
</tr>
<tr>
<td>Offshore production</td>
<td>29</td>
</tr>
<tr>
<td>Atmospheric</td>
<td>20</td>
</tr>
<tr>
<td>Coastal surge</td>
<td>14</td>
</tr>
<tr>
<td>Coastal refineries</td>
<td>6</td>
</tr>
<tr>
<td>Oil Terminals</td>
<td>0.8</td>
</tr>
<tr>
<td>Industrial effluents to sea</td>
<td>9</td>
</tr>
<tr>
<td>Natural seepage</td>
<td>0.8</td>
</tr>
</tbody>
</table>

Much of the assessment of the effects of oil pollution has arisen from marine circumstances - coastal and estuarine. This has resulted from tanker accidents and because oil refineries are located on coasts and estuaries for obvious reasons.

QUALITY LIMITS AND CONTROL

Effects of Pollution

Petrochemicals in the aquatic environment occur in six modes.

(i) Microlayer at the surface of water - this could be monomolecular
(ii) Free droplets
(iii) Dispersed emulsion
(iv) Separated emulsion (mousse)
(v) Absorbed or adsorbed onto solid matter, eg. beach detritus, river muds and sewage solids
(vi) Solution.

The impact will be different in each circumstance.
Petrochemicals may have three effects.

1. **Interfacial effects**
2. **Aesthetic impact**
3. **Direct toxicity.**

The interfacial effects are such that the transport of a given species between phases is inhibited. Examples are the resistance to contact of oil-contaminated electrodes (and hence failure of electrode controlled water pumps) and a reduction of oxygen transfer at a water interface (Belolvanenko and Mironov, 1979). This can have environmental consequences and can inhibit aerobic biological effluent treatment processes. The smothering effect on seashore life can be serious in the case of marine pollution. Suffering, oil-coated sea birds gain very powerful public sympathy during major incidents. For instance, the Torrey Canyon incident in the UK when 117,000 tons of crude oil were discharged, killed 30,000 birds (Wardley-Smith, 1983 McIntyre, 1987) and created a lasting emotional precedent.

Aesthetic effects arise from the same interfacial phenomena. Oil floats, causing iridescence, coats plants and animals, deposits on beaches leaving an unsightly appearance and is a potential source of contamination of clothes and so on.

Oil may form true solutions, for instance at less than 1 mg/l, particularly the aromatic components (Jeltes, 1974). However, under quiescent conditions, mobile oils tend to concentrate at the surface giving rise to readily visible effects. 0.04 ml/m² (4 x 10⁻⁵mm thick) is just detectable on a water surface; 0.3 ml/m² gives obvious bands of colour and 2 ml/m² (2 x 10⁻³mm thick) produces a dark colour (CONCAWE, 1974).

However, this situation is rather complicated with several equilibria involved. Oil may become adsorbed and absorbed onto mineral and organic material present. Further, emulsions may be formed by agitation. These may be of sufficient quantity to separate and give rise to coherent very stable matrices which can then entrain solid matter such as seaweed, feathers, sand or faeces (Wardley-Smith, 1983).

These are stabilized by trace constituents such as asphaltenes, aromatics, additives and so on. Similar emulsions cannot be effected with highly refined products. These have become known as "chocolate mousses" (from their appearance) for crude and fuel oils. Similar effects have been found with motor lubricating oils in sewers. Experiments have shown that motor oil forms an emulsion containing 42% oil - the viscosity being very much less and non-newtonian (increases with shear force) thus explaining the difficulties which occur in siphons and in pumping oil-contaminated sewage. This can make wastewater management unpleasant and difficult for operatives (Matthews, 1986).

In the extreme, if excessive amounts of volatile petrochemicals are discharged into sewers there can be an explosion and fire risk. Stories of a man throwing a cigarette end into a sewer and causing an explosion from petrol vapour - lifting off manhole covers - are apocryphal but have a basis of truth.

The toxicity of petrochemicals is a massive subject which has been researched and reported extensively. The general nature of oil and individual constituents varies widely and hence this affects the extent of the toxicity. The extent of the effect will depend on the nature of the receiving environment and of the oil itself. It is known that oil "weathers" and changes composition by volatilisation, biodegradation and oxidation (Little, 1981; Albages and Cuberes, 1980). Hence the toxicity of a fresh oil may be different to that of weathered oil and this has given problems in the correlation of laboratory tests and field observations. In the case of the oil spillages, where dispersants are used, the toxicity of the dispersant itself and the dispersed oil emulsion may be significant (Norton and Franklin, 1980).

The impact of a refinery effluent will be regular (apart from spillages) and, therefore, different to that of tanker accidents.

It has been reported that, for instance, a refinery effluent in a fairly sheltered rocky coastal bay in the UK had reduced the abundance of limpets (conical marine gastropods) with the consequent increase in seaweed (Wardley-Smith, 1983). Top shells, winkles and barnacles were also reduced in numbers (Wardley-Smith, 1981). In most cases it is the impact of the effluent on the ecosystem and the population changes which are of concern. One change causes a chain reaction (Clark, 1982).
The effect may well be directly in the water column but accumulation of oil and heavy metals in the sediments around the end of the discharge point may cause long lasting perturbation of the benthic community by direct toxicity or by the formation of anoxic conditions.

### TABLE 2 Some Limits from EC Directives of Relevance to Refinery Effluents

<table>
<thead>
<tr>
<th>Directive</th>
<th>Oil</th>
<th>Phenol</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Imperative</td>
<td>Guide</td>
</tr>
<tr>
<td>1976 &quot;Bathing Water&quot;</td>
<td>No film</td>
<td>0.3 mg/l</td>
</tr>
<tr>
<td></td>
<td>0.1, 0.2, 0.3 mg/l</td>
<td>0.001, 0.005, 0.1 mg/l</td>
</tr>
<tr>
<td>1978 &quot;Freshwater Fish Water&quot;</td>
<td>No film, no effect on fish flavour, no harmful effects</td>
<td>-</td>
</tr>
<tr>
<td>1979 &quot;Shellfish Water&quot;</td>
<td>No film, no film on shells, no harmful effects.</td>
<td>-</td>
</tr>
<tr>
<td>1980 &quot;Drinking Water&quot;</td>
<td>Pet. ether ext.</td>
<td>0.5 μg/l</td>
</tr>
<tr>
<td></td>
<td>10 μg/l</td>
<td></td>
</tr>
</tbody>
</table>

The EQO requires an environmental quality criterion to be met in all circumstances, such as exists for cadmium, mercury, lindane, carbon tetrachloride, pentachlorophenol and DDT under List I of the 1976 EC Dangerous Substances Directive and defined by the European Commission (WAA, 1986a). The criteria may take account of the nature and use of the water; values may be defined, as have been implemented so far in the UK for zinc, copper, nickel, lead, chromium and arsenic (DOE, 1985) under List II of the 1976 Directive and have been included in the other use-related Directives. Few actual values for petroleum and petroleum products have been provided by the European Community or by the UK Government (see Table 2).

Petroleum and petroleum products are List I materials but will be treated as List II until List I values are introduced. The EC has a list of 129 priority substances of which several are petrochemicals, such as benzene, toluene and xylenes (Wolff, 1985).

However, the UK government is a signatory of the International Paris Convention for the Prevention of Pollution from Land Based Sources (for the North East Atlantic) and the Commission is working towards a limit of 15 mg/l on discharges from reception facilities (Wedege, 1987). Whilst on the subject of international efforts to control the pollution of the sea and ships, and the marine dispersal of wastes there are several international conventions such as the London Convention, the Oslo Convention, the MARPOL Convention, and the Barcelona Convention, affecting European Waters and a proposed EC Directive.

The concept of environmental quality objectives requires the definition of a "mixing zone" (WAA, 1986b). Inside this zone the quality criteria will be exceeded and there may or may not be biological consequences - this will depend on how much safety margin the criteria have. The size of the zone will depend on social acceptability, economics, environmental and conservation value and so on. In tidal waters this will require modelling and the zone will be a statistical concept and will be associated with a zone of biological impact, if any.

EC Directives have been in harmony with developments in the UK in the use of percentile criteria - particularly 95 percentile values. Absolute values have no real meaning in practice, particularly where the criteria may have statutory force.

This percentile concept has been translated, in part, to effluent discharges, although control and monitoring systems have to become more sophisticated to reflect this (Ellis, 1986). The translation of environmental criteria to the acceptable values defined in

* EQO - Environmental Quality Objective.
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Discharge licences, called consents in the UK, have needed the development of statistical models best used on computers (Barnden et al., 1986; WAA 1986a).

Chronic mortality of zooplankton or benthic fauna can result in an increase of the microalgal biomass in the system as the reduction of grazing pressure upon algae exceeds the inhibition of the primary productivity. Such an increase of marine algae, generally of microflagellates, has also been observed in the long term after oil spills (Clark, 1982).

In the case of refineries discharging to marine waters it must be noted that the discharge is usually of fresh water and, by reducing the salinity of an area of the receiving water, the biological status of that area is affected.

Plants may be affected, for instance, a refinery effluent in the south of England caused devegetation of a salt marsh system but more than 3 fold improvement of the effluent to 10mg/l oil permitted re-establishment of vegetation although the animal communities are recovering more slowly, possibly because of the continued presence of oil in the sediments (Clark, 1982).

These biological problems tend to relate to marine systems particularly in the UK but similar effects are observed in freshwaters although possibly to a lesser extent. It is possible that many fresh water species are more tolerant of oil contamination than similar marine species although this should not be taken as a general rule (Lock et al., 1981).

Marine waters are generally a more productive food source than fresh waters and hence the impact of refinery effluents is of importance in terms of public health and local economics. Even if the marine communities survive, albeit at reduced productivity, it may well be that the shellfish or pelagic fish become tainted or contaminated. There is no evidence, however, that oil tainted sea food has accumulated chemicals, such as polynuclear aromatic hydrocarbons, to unacceptable levels and shellfish at least will lose the tainting if placed in clean water. Contamination of fish could be more long lasting. The analysis of fish livers provides a useful indication as well as being an important health check - for fish oil is often extracted from livers as a source of vitamins; contaminated livers have been found in cod near oil production platforms in the North Sea (Drangsholt et al., 1987). Of course, the accumulation of heavy metals in shellfish and fish is a well established phenomenon.

The information summarised so far has related to environmental water, particularly marine waters, but if refinery effluents are disposed of by percolation into land there is a risk that groundwater may become contaminated. Although there may not be immediate environmental consequences, (apart from the possibility of polluted spring water), the groundwater is rendered unusable as an irrigation or potable water source (Yazicigil and Sendlein, 1981).

Where the petrochemical effluent is discharged to public sewers and thence to sewage treatment works care has to be exercised. Volatile constituents such as benzene, toluene, xylenes, cyclohexane, and so on, can form toxic as well as explosive atmospheres (Matthews, 1975a). The oil and other constituents may affect the efficiency of the biological treatment systems, the quality, and hence disposability, of the sewage sludge, and of course the quality of the treated effluent, either directly by passage of a portion through the treatment process or by causing failure of the treatment process. Of course, acclimatization of the aerobic treatment processes can ameliorate, to some extent, the loss of efficiency (Matthews, 1975b).

Approaches to Control Philosophies and Practices

In essence there are two approaches - that known as the uniform emission standard (UES) and that known as the local emission standard (LES). The first approach, adopted by many countries, involves defining the quality of effluents as a common standard (WRc, 1976). It might go as far as specifying the quality of effluents as a common standard (WRc, 1976). It might go as far as specifying the type of treatment process which the effluent has passed through, (such as is the case in the USA). The second approach defines an environmental quality objective (EQO) for a receiving water. The quality of the effluent discharged to the water will vary according to local circumstances, so that the EQO is not breached (WRc, 1976).

The UK practice for quality control has been evolving towards the EQO approach for many years - the famous Royal Commission on Sewage Disposal at the beginning of this century set precedents. However, there is scope for the use of both approaches according to needs (House of Lords, 1985). The contrast between UES and LES has been highlighted in the water quality Directives issued by the European Community, particularly that for dangerous substances in...
In day to day practice the UK quality managers (in water authorities in England and Wales) draw on toxicological data available in scientific literature and advice from the toxicological advisory service at the Water Research Centre. For instance, it is suggested that a value in excess of about 20 \( \mu \text{g/l} \) of oil causes problems with planktonic communities (McIntyre, 1987). These levels of contamination are usually only found at the end of a discharge pipe. In general there does not seem to be evidence for permanent damage to open sea pelagic ecosystems, but in more enclosed coastal areas, subject to chronic oil and industrial effluent contamination there may be greater impact. However, this should not be taken as an absolute target as evidence exists for toxic effects in some circumstances at these concentrations (Scholten and Kuiper, 1987).

A common target, which can be seen from the requirements of certain EC Directives, is avoidance of visible oil and information on suitable values has been given earlier in this paper.

Where petrochemical effluents are discharged to public sewerage systems, care has to be exercised to ensure hazardous atmospheres are not formed in sewers and pumping stations. This can be achieved by using values defined for safe atmospheres in the ordinary workplace and relating these back to the acceptable concentrations in sewage by the use of Henry's Law. This acts as the quality target which can then be used as a basis for the calculation of the industrial effluent limit (Matthews, 1975a). It has been found in the UK that to avoid problems with oily blockages the best practice is to have a common limit for all discharges within the sewer catchment - this is often 300–500 mg/l oil. It has been found that 50 mg/l is the maximum which can be accepted in the sewage biological treatment; care has to be exercised to ensure that the sludge does not become too oily (Matthews, 1975b). The sewage effluent has to meet the river quality target. Of course, the management of oil in sewage treatment works and rivers is made difficult by all the unidentified "diffuse" sources.

It has been found that the mean hydrocarbon content of UK rivers is 100 \( \mu \text{g/l} \) (by comparison to a range in the North Sea of 0.5 to 3 \( \mu \text{g/l} \) and 10 – 80 \( \mu \text{g/l} \) inside the major English estuaries with refineries draining to the North Sea). Sediments in clean areas of the North Sea contain up to 160 mg/kg oil but there are contaminated estuaries containing several hundreds – even thousands of mg/kg (McIntyre, 1987). A survey of sewage treatment works in 1983 showed that crude sewage in England and Wales contained typically 6 mg/l and final effluents about 1 mg/l. Wet sludges contained typically about 600 mg/l oil (Gardiner, 1983).

**Petrochemical Effluents - Quality and Control**

This paper does not seek to detail different petrochemical processes. It is known that the product water from processes may contain phenols, oils, solvents, ammonia, hydrogen sulphide, acid or alkalis and heavy metals. These may be combined and dealt with at a central treatment plant on the refinery. However, it often makes sense to keep the clean waste process water separate from the dirty water in order to maximise the efficiency of treatment.

As with all industrial effluents, good husbandry and minimisation of process and cooling water is the key to successful control. The processes needed are varied – requiring, as needed, chemical treatment, aeration, oil removal by separators (tanks, plate interceptors etc) sedimentation, filtration, air flotation, and biological treatment. In 1984 a CONCAWE survey confirmed that since 1969 there had been an overall 50% improvement in refinery effluents in Europe although there has been a decline in total refinery capacity at the same time. Almost three quarters of the refineries now provide gravity separation, and some form of advanced treatment followed by biological treatment.

**Monitoring**

**Sampling**

Sampling accurately is always important but in the case of oil-contaminated samples the problems are greater, the substrate being a two phase system when there is excessive contamination.
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In the case of the large discharges with potential significant impact, continuous monitors combine sampling and analysis. Volumetric monitors have been developed, based on UV absorption and fluorescence (Anon, 1980). However, systems based on electrical conductance, light reflectance and infra-red spectrophotometry and spectroradiometry have been suggested and marketed with varying degrees of success (Matthews, 1975a).

Standard sampling techniques have been applied to refinery effluents. However, special sets of apparatus have been designed to give a "core" sample in which the surface area is defined. Hence, assuming that the oil determinand in the total sample is concentrated at the surface, a measurement of surface concentration in slicks may be obtained. When a "grab" sample has been taken it should be placed in a clear glass stoppered bottle. In order to avoid loss of oil accumulated at the surface it should be filled completely. Losses can occur in sample transfer and by adsorption and absorption onto the sample and sample bottle surface. The oil so lost may be recovered in the laboratory in some instances. When there is a chance of biodegradation occurring and immediate analysis is not possible, it is advisable to "fix" the sample with acid or the solvent to be used in analysis (Matthews, 1975a; SCA, 1983).

Analysis

The effluent may be analysed for general organic contamination (such as COD and BOD), phenols, sulphide, ammonia, metals, acidity/alkalinity, solvents and petroleum and petroleum products and by-products etc. by standard methods. These involve a variety of classical techniques as well as most of the most sophisticated instrumental techniques. Chromatography of one sort or another is used to sort out complex mixtures. However, the analysis of the material loosely called "oil" presents the greatest analytical problems because of the complex nature of the determinand and hence the values observed are influenced and defined by the analytical method used.

A common outline procedure involves the oil being first separated by extraction by a solvent such as a petroleum spirit, hexane, pentane, carbon tetrachloride or trichloro-trifluoro-ethane (TTE). The extract, after drying and clean-up with alumina or kieselguhr, may then be examined quantitatively for hydrocarbon content by infra-red spectrophotometry, gravimetry or fluorescence spectrophotometry or even mass spectrometry.

The pollutant may be present in such gross quantities as to circumvent this analytical procedure and physical assessment may suffice. Oil - isolated by whatever method - may be analysed for its characteristics using classical analysis (for instance for fat content, unsaturation, acid solubility and so on), infra-red and ultra-violet fluorescence spectrophotometry, gas liquid chromatography (low and high performance separation), mass spectrometry, thin layer chromatography, and, when there has not been extraction, metals, sediments and even water in the case of emulsions. However, it must be remembered that standard techniques for routine work in operational laboratories must be relatively simple and not require sophisticated knowledge. Characterisation and quantification should be possible with the aid of standards, written guidance and some experience. This is true when water analysts are dealing with oil pollutants.

In the UK, the government's Standing Committee of Analysts has produced a series of standard methods for this purpose (SCA, 1978–1985). Guidance is also provided by the Institute of Petroleum in its publications (Institute of Petroleum, 1974).

With the international nature of oil pollution (by international companies often in international waters), the International Standards Organisation, International Marine Organisation and International Conference on Oil Pollution are producing reference methods. An important procedure is that of TTE extraction followed either by infra-red spectrophotometry (0.1 mg/l - 50 mg/l) and gravimetry (5 - 1000 mg/l) (SCA, 1983).

CONCLUSIONS

In general, petrochemical effluents are causing much fewer problems than was the case a decade or two ago.

This improvement has been achieved by close co-operation between the oil and water industries. In the UK this has been aided by the regional and integrated nature of water management of river basins. Clear responsibilities and laws are essential.
Extensive quality and toxicological information is vital to assist in the decision as to what effluent target should be set. Whilst this paper has concentrated on the impact of refinery effluents it must not be forgotten that contributions may be made from the transport and unloading of crude oil and refined products. The general use of petrochemicals influences the quality particularly of fresh waters.

Accurate monitoring programmes and clear analytical methods commonly used are essential in the understanding of environmental information but the mistake must never be made of setting standards with data derived from one method and then monitoring against that standard using a method with different performance characteristics.

Oil pollution has not been in the public mind for some time in the UK but constant vigilance by authorities for good discharge quality and avoidance of polluting entries - spillages and so on, is vital in a world with an increasing demand for better environmental protection.

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REFERENCES


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