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Oil refineries: a review of their ecological impacts on the aquatic environment

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Abstract

Pollution of the aquatic environment occurs from many different sources including from oil refineries. Oil refinery effluents contain many different chemicals at different concentrations including ammonia, sulphides, phenol and hydrocarbons. The exact composition cannot however be generalised as it depends on the refinery and which units are in operation at any specific time. It is therefore difficult to predict what effects the effluent may have on the environment. Toxicity tests have shown that most refinery effluents are toxic but to varying extents. Some species are more sensitive and the toxicity may vary throughout the life cycle. Sublethal tests have found that not only can the effluents be lethal but also they can often have sublethal effects on growth and reproduction. Field studies have shown that oil refinery effluents often have an impact on the fauna, which is usually restricted to the area close to the outfall. The extent of the effect is dependent on the effluent composition, the outfall's position and the state of the recipient environment. It is possible to detect two effects that oil refinery effluent has on the environment. Firstly it has a toxic effect close to the outfall, which is seen by the absence of all or most species. Secondly there is an enrichment effect which can be distinguished as a peak in the abundance or biomass. These effects are not limited to just oil refinery effluents, which makes it difficult to distinguish the effects an oil refinery effluent has from other pollution sources. The discharge from oil refineries has reduced in quantity and toxicity over recent decades, allowing many impacted environments in estuaries and coasts to make a substantial recovery.

Keywords: oil refinery; effluent; petrochemicals; estuaries; toxicity; recovery

1. Introduction

The condition and health of the aquatic environment is constantly being monitored so that the effects of pollution can be better understood and its impact reduced. Pollution of the aquatic environment has many sources such as sewage disposal, land run off, atmospheric fallout and industrial wastes. This review concentrates on the impact of oil refinery wastes.

The total quantity of aqueous effluent that is being discharged by oil refineries has decreased over the years, for example European refineries discharged 3119×10^6 t year^{-1} from 80 refineries in 1969 reducing to 2543×10^6 t year^{-1} from 84 refineries in 2000 (Table 1). The decrease between 1974 and 1978 is thought to be due to more refineries using air cooling and recirculating cooling water systems. Refineries can be categorised into four different types depending on their complexity (Concawe, 2004; Table 2). Over the years the complexity of refineries has increased and since 1969 there has been the introduction of more effective treatment systems. The three main treatment processes for effluent before its

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Table 1
Effluent discharge data for European refineries (from Concawe, 2004)

Year of survey	1969	1974	1978	1981	1984	1987	1990	1993	1997	2000
Number of refineries reporting these data	80	108	111	104	85	89	95	95	105	84
Total aqueous effluent (10^6 t year^{-1})	3119	3460	2938	2395	1934	1750	1782	2670	2942	2543
Aqueous effluent (t/t capacity)	8	4.9	3.9	3.4	3.2	3	3	4.3	4.4	4.5
Aqueous effluent (t/t oil processed)	nd	nd	5.4	5.4	4.6	3.9	3.5	4.8	4.7	4.9

discharge are gravity separation (API separators, tank separation), advanced treatment (flocculation, sedimentation, filtration) and biological treatment (biofilters, activated sludge, aerated ponds) (Concawe, 2004). The percentage of refineries that have all three treatment processes has increased over the years from only 23% (of 82 refineries) in 1969 to 91% (of 84 refineries) in 2000 (Table 3).

As not all refineries have the same processes, the effluents that are produced will have different chemical compositions depending on the type of treatment they receive (Lehtinen, 1986). Petroleum refinery wastewaters are made up of many different chemicals which include oil and greases, phenols (creosols and xylenols), sulphides, ammonia, suspended solids, cyanides, nitrogen compounds and heavy metals like chromium, iron, nickel, copper, molybdenum, selenium, vanadium and zinc (Cote, 1976). Oil consists of five types of components, saturated non-cyclic hydrocarbons (paraffins), cyclic hydrocarbons (cycloalkanes), olefinic hydrocarbons (alkenes), aromatics and non-hydrocarbons (sulphur compounds, nitrogen-oxygen compounds and heavy metals) (Cote, 1976). Refinery effluents tend to have fewer of the lighter hydrocarbons than crude oil but more polycyclic aromatics which tend to be more toxic and more persistent in the environment (Tatem et al., 1978).

Since 1969, the amount of oil that is discharged in the refinery effluents of Europe has decreased from 44,000 t year^{-1} from 73 refineries to 747 t year^{-1} from 84 refineries in 2000 (Fig. 1). The discharge levels of ammonia and phenols have also reduced by 45% and 60%, respectively from 1993 to 2000 (Table 4). Burks (1982) noted that the number of components in the original crude oil stock, plus the resultants from the fractionation process, plus any addition of chemical additives within the refinery operations determine the number of components within a wastewater. This means that each effluent is generally unique and can vary on a daily basis depending on which units within the refinery are in operation. This makes it hard to generalise on the effects of oil refinery effluents.

Table 2
Classification of refineries (from Concawe, 2004)

Type I	Simple (non-conversion) refinery: composed of crude oil distillation; reforming; treatment of distillate products, including desulphurisation and/or other quality improvement processes (i.e. isomerisation or speciality manufacturing)
Type II	Type I plus catalytic cracking and/or thermal cracking and/or hydrocracking
Type III	Type II plus steam cracking and/or lubricant production within the refinery fence
Type IV	Refineries not in above categories, e.g. those producing only bitumen, lubes, etc. which import their feedstocks from other sources

2. Fate of the effluent

The fate of oil refinery effluent once it is discharged into the environment depends on the conditions and hydrodynamics of the receiving water. The effluent is inevitably diluted within the receiving water but to what extent depends on the size of the recipient and where the outfall is located, whether it is intertidal or subtidal. Grahl-Nielsen (1987) dyed the discharge water from an offshore operation and found that the discharge was unevenly distributed in the recipient waters.

Most studies on the fate of refinery wastes just consider the hydrocarbons within the effluent. The volatile compounds are lost from the water column through weathering (Cranthorne et al., 1989). The remaining compounds undergo sedimentation and biodegradation. Knap and Williams (1982) found that the most important removal mechanism was sedimentation and that in Southampton Water 70% of the hydrocarbons were found in the sediments after 1 h. Compounds with high water solubility such as aromatics were absorbed slower than non-polar compounds like aliphatics. In Southampton Water biodegradation occurred rapidly, hydrocarbon concentrations were reduced by 70% after 40 days, much faster than in other areas. The increased speed of biodegradation was attributed to the substantial population of oil degraders in the area that had accumulated over the 50 years of chronic discharge. Most of the hydrocarbons that are degraded are lower molecular weight aliphatic fractions. This means that over time hydrocarbon concentrations

Table 3
Waste water treatment systems in oil refineries in Europe (from Concawe, 2004)

Year of survey	Number of refineries reporting these data	Refineries equipped with:					
		Gravity separation only (G)		G plus advanced treatment only (GA)		G plus biological treatment (GAB)[a]	
		No.	%	No.	%	No.	%
1969	82	51	62	12	15	19	23
1974	112	47	42	21	19	44	39
1978	109	40	37	15	14	54	49
1981	105	31	30	19	18	55	52
1984	85	15	18	8	9	62	73
1987	89	13	15	10	11	66	74
1990	95	7	7	12	13	76	80
1993	95	6	6	8	8	81	86
1997	105	6	6	8	8	91	86
2000	84	3	4	4	5	77	91

[a] Note that for 1997 and 2000 only, GAB also includes additional polishing or offsite biological treatment for some refineries.

do decrease but due to the constant effluent discharge they are always being replenished. Therefore if the discharges were to cease or the hydrocarbon concentration within effluents were to be reduced then there is the potential for the hydrocarbon concentrations to decrease to lower levels within the sediment.

Le Dreau et al. (1997) observed that around a petroleum refinery in the Gulf of Fos (South France) there were three zones of contamination of the sediment. Firstly a highly contaminated zone near the refinery (50 g kg^{-1} sediment dry weight), followed by a less contaminated zone in the deep creek ($\sim$3 g kg^{-1} sediment dry weight), with a final slightly contaminated zone in the open sea ($\sim$0.1 g kg^{-1} sediment dry weight). Other studies have also shown that the area of high contamination is often localised to the vicinity of the outfall and decreases with distance (Knap et al., 1982; Armannsson et al., 1985; Moore et al., 1987; Talsi, 1987). The hydrocarbons seem to sediment out near to the discharge point.

There also seems to be a pattern of hydrocarbon distribution with depth but this varies depending on the history of the discharge and sedimentation rates of the area concerned. Talsi (1987) observed that around the Neste Oy's oil refinery in Finland the maximum concentration of oil was at 4–14 cm and that there seemed to be no further degradation at this depth. In Narragansett Bay it was discovered that the hydrocarbon concentration decreased with depth and that with increasing depth a greater percentage of the oil was of biogenic origin (Van Vleet and Quinn, 1978). This would suggest that in this area degradation of the light fractions was occurring within the sediment leaving the heavier biogenic hydrocarbons, which could be due to a slow sedimentation rate. The pattern of the concentration of contaminants with depth of the sediment can also be linked to the history of the inputs to the area. Cranthorne et al. (1989) found that at Kinneil in the Forth Estuary the aliphatic concentration increased with depth, which could be a reflection of the reduced hydrocarbon content of the effluent over the years. Knap et al. (1982) observed that in Southampton Water there was a distinct oil horizon within a core at 90–100 cm depth, which they attributed to the expansion of the oil refinery in this area in around 1950 and a subsequent reduction in discharges. This again shows that no generalisations can be made between different areas as to the fate of the components in the effluent.

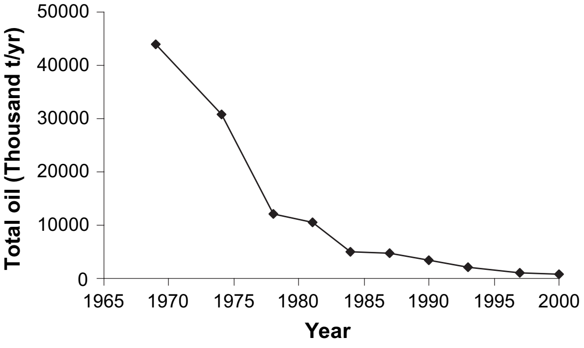

Fig. 1. Total oil content of the effluent from refineries in Europe (from Concawe, 2004).

Table 4
Discharge rates of ammonia and phenols from European refineries (adapted from Concawe, 2004)

Year		Ammonia	Phenols
1993	No. of refineries reporting this data	82	77
	Tonnes/year discharged	5202	179
1997	No. of refineries reporting this data	82	73
	Tonnes/year discharged	3210	161
2000	No. of refineries reporting this data	46	55
	Tonnes/year discharged	1715	61
1993–2000	Percentage reduction on throughput	45	60

3. Toxicity tests

There are many different ways of testing the toxicity of different compounds but there are two main types of tests. Firstly, the acute lethal test which usually lasts 96 h. The aim of this type of test is to find out the lethal concentration of a substance. Secondly, there are sublethal tests. These can take many forms but basically test for any sublethal reactions that a substance may cause that could cause a problem for the individual and/or the population over a long period of exposure. Measurements of sublethal effects that are often used are respiration rate, growth rate, reproductive success and behavioural changes. Acute tests are the most common but sublethal tests are also important especially when looking at the impact of a chronic problem like refinery effluents. Many different species have been used to look at the toxicity of oil refinery effluents including species of fish, crustaceans, plankton and algae.

The toxicity of oil refinery effluent is dependent on a number of factors. The volume, quality, salinity and variability of the discharge, the siting of the outfall, the physical and chemical conditions of the discharge area, the proximity of other effluents and pollutants and the biological condition of the discharge area (Concawe, 1979). The different components of the refinery effluent can have varying effects and toxicities (Smith, 1974). The oil in the refinery effluent can affect marine organisms in a number of different ways. It can kill them directly through coating and asphyxiation, contact poisoning, or through exposure to water-soluble components. It can also cause the destruction of more sensitive juveniles or of the food organisms therefore wiping out a population. Lastly oil is capable of causing sublethal and stress effects, carcinogenic and mutagenic effects and can effect the behaviour of individuals (Cote, 1976). The toxicity of ammonia is dependent on pH, oxygen concentration and temperature (Cote, 1976). With increasing pH (Burks, 1982) and decreasing O_2 (Cote, 1976) ammonia becomes more toxic. Ammonia is removed by bacteria in well-oxygenated areas and is therefore not likely to be accumulated by marine organisms (Concawe, 1979). Sulphides on the other hand are also removed by bacteria (Concawe, 1979) but have the opposite relationship with pH. The toxicity of sulphides increases with decreasing pH. Cyanides are also very toxic to marine organisms and the toxicity is affected by synergism with other compounds like ammonia and zinc. Cyanide affects the transport of oxygen from the blood to the tissues (Cote, 1976). Phenols on the other hand are less toxic and are readily biodegraded by bacteria within 200 min given the right conditions (Cote, 1976). Lastly heavy metals can have toxic effects. The different metals have varying effects that also vary with temperature, salinity, pH and valence and can act synergistically with one another (McLusky et al., 1986). The exact effects of refinery effluent and its constituents thus can and do vary between species and from location to location.

3.1. Phytoplankton and algae

There are very few studies that look at the effects of refinery effluent or its components on algae. Saha and Konar (1985) used 90-day toxicity tests on phytoplankton. It was found that at the highest concentration tested (5.84% refinery effluent) the phytoplankton numbers decreased.

The sublethal effects of the effluent from two Ontario (Canada) refineries were examined using three species of algae (Sherry et al., 1994). The refinery effluent inhibited the growth of the alga *Selarolstrom apricorntum* and the duckweed *Lemna gibba*. It also reduced the germination in *Lactuca* seed by 15%. More studies are needed on the effects on algae, as they are an important link in the food chain. Reduced productivity of phytoplankton and/or algae will have a knock on effect to the other organisms in the environment, such as crustaceans and fish. Studies of the microalgae living in an oil refinery effluent holding pond have shown that selection can occur favouring resistant genotypes within a population and selection among species can result in changes in community structure (Joseph and Joseph, 2002).

3.2. Invertebrates

Many studies have used freshwater and marine invertebrates as test organisms to observe the effects of refinery effluent and its individual components. Crustaceans seem to be more sensitive than other aquatic organisms. Tests of the toxicity of refinery effluent from BP Grangemouth on four species of marine invertebrate found that the most sensitive to the effluent was *Praunus flexuosus* > *Corophium volutator* > *Macoma balthica* > *Hydrobia ulvae*, using 24 and 48 h LC50 tests (Smith, personal communication). Other studies have found marine/estuarine species to be more sensitive than fresh water species (Scheier et al., 1979; Bleckmann et al., 1995).

The conditions of the toxicity tests are also very important. Using sediment within a toxicity experiment has varied effects. Smith (personal communication) found that during acute toxicity tests the presence of a substrate caused enhanced survival for all four species (*Praunus flexuosus*, *Corophium volutator*, *Macoma balthica*, and *Hydrobia ulvae*).Contrary to this Scheier et al. (1979) found that the addition of sediment actually increased the toxicity of the refinery effluent to the tadpole snail and grass shrimp. The toxicity of the effluent was also found to change with storage. There was a significant loss in toxicity when the effluent was stored for 24 h before use in an experiment (Bleckmann et al., 1995).

Sublethal toxicity tests on invertebrates have concentrated on the changes in reproductive success. Norbert-King and Mount (1986) observed that *Ceriodaphnia* in diluted refinery wastewater produced fewer young per female than the controls. Buikema et al. (1981) also found that an artificial refinery mixture (ARM) decreased the egg production and the number of broods in the estuarine crustacean *Mysidopsis bahia*. The effects of the two effluents that were discharged from BP Grangemouth on four marine invertebrates has been compared. It was found that the petrochemical effluent was more toxic than the oil refinery effluent (Smith, personal communication). This suggests that it is not necessarily the oil, but may be some of the other chemicals in the petrochemical waste that have the greatest toxic effects.

Some studies have tried to identify the relative toxicity of individual components so that the chemical or group of chemicals that cause the toxic effects can be determined. Hall et al. (1978) investigated the toxicity of six components of refinery effluents on the Grass shrimp *Palaemonetes pugio* using 96 h tests. The order of toxicity was determined starting with the most toxic. No 2 fuel oil > sulphide > ammonia > phenol > chromium > kalinite. Fuel oil was also found to be the most toxic component of an ARM (Buikema et al., 1981). Storey (personal communication) also observed that ammonia was more toxic than phenol to *Corophium volutator*, whereas oil was found to have no acute toxic effect. Reece and Burks (1985) tried to isolate the fractions of refinery wastewaters that were lethal to *Daphnia magna* using stepwise treatments and toxicity tests. The components that were found to be most toxic were the steam volatile, base neutral, aromatic compounds. Eleven polycyclic aromatic hydrocarbons (PAHs) were identified (Table 5) but it was noted that although all these compounds were toxic they must be working in an additive or synergistic manner to produce the toxic effects shown in the experiments. The test conditions also affect the toxicity of the individual components. Low salinity was found to enhance the toxicity of ammonia for *C. volutator* (Storey, personal communication). Hall et al. (1978) discovered that temperature was the most important environmental variable for *P. pugio* whereas light intensity, photoperiod and salinity had no effect. Animals from different locations and different genera showed the same effects, but larvae were more sensitive than adults (Hall et al., 1978).

Table 5
The 11 identified polyaromatic hydrocarbons that were lethal to *Daphnia magna* (adapted from Reece and Burks, 1985)

Polyaromatic hydrocarbons
Dihydromethylphenylbenzofuran
C_2-(pyrene/fluorcinthene)
Benzofluorene
Methyl benzofluorene
Chrysene/benzanthrene
C_2-benzofluorene
Methyl (chrysene/benzanthracene)
C_3-benzofluorene
C_2-(chrysene/benzofluoranthene)
Benzopyrene/benzofluoranthene
Methyl (benzopyrene/benzofluoranthene)

Sublethal effects of effluent components to changes in reproductive success have also been considered. Buikema et al. (1981)) looked at the effects of ammonia, phenol, chromate and fuel oil on the reproduction and growth of *Mysidopsis bahia*. No animals that were exposed to ammonia survived to reproductive maturity. Those animals exposed to phenol, chromate and fuel oil experienced reproductive impairment. Phenol also caused growth inhibition whereas chromate caused the animals to swim in spirals. Changes in behaviour have also been noticed in other studies. During 96 h tests zooplankton (*Daphnia magna*) became erratic and uncoordinated in the water column when exposed to *n*-heptane, cyclohexane, benzene, diesel oil, mobile oil and oil refinery effluent (Das and Konar, 1988).

Genotoxic effects have been evaluated in the cells of bivalve and gastropod molluscs inhabiting different sites of Klaipeda port area in Lithuania (Barsiene, 2002), with the highest genotoxicity levels being found in the zone of sewage effluents from Palanga town and effluents from the Mazeikai oil refinery.

3.3. Fish

Fish have been used for the toxicity testing of oil refinery effluent in many different studies, most of which have looked at sublethal effects. Many different species of fish have been tested over the years. Irwin (1965) used acute toxicity tests to determine the sensitivity of 57 species of fish to refinery wastewater. It was discovered that there was a variation both within and between species. The guppy (*Libestes reticulatus*) was the most resistant of the 57 species that were tested. Clemens and Summers (1953) observed the effects of refinery effluent on five species of fish and found that the goldfish (33.1%) was the most resistant followed by the green sunfish (23.3%), red shiners (18.8%), golden shiners (18.7%) and lastly fathead minnows (17.0%).

Two experiments have looked at the effects of Haldia refinery effluent on *Tilapia mossambica* using 96 h toxicity tests. The LC50 (median lethal concentration) value of refinery effluent was 54%. At 80–100% refinery effluent the fish usually died within 24 h showing signs of respiratory distress, surfacing and secretion of mucus (Saha and Konar, 1984a). Saha and Konar (1984b) observed the respiratory and feeding rates of *T. mossambica* exposed to different concentrations of effluent. At

2.10% and 5.84% of refinery effluent there was an increase in respiratory rate but no effect on feeding rate.

Saha and Konar (1984b) used longer 90 day toxicity tests to look at several sublethal effects on *Tilapia mossambica*. None of the fish died over the 90 day experiments. At 2.10% refinery effluent, the fish yield was significantly reduced, the fish showed signs of respiratory distress and hampered growth. At 0.58% and 5.84% refinery effluent, the maturity index for females varied significantly from the controls. Fecundity of the fish in contact to refinery effluent was discovered to decrease but not significantly. Rowe et al. (1983a) also found that fecundity was affected by refinery wastewater. In 28% effluent the fish produced fewer eggs per spawn, spawned less frequently and had delayed spawning. They also showed that the 1st and 2nd generations were smaller and that spinal curvature was present in the 2nd generation and all fish showed haemorrhaging of the fins. Rainbow trout have been observed to have erosion of the caudal fins when in contact with 31% refinery effluent (Rowe et al., 1983b). The growth of rainbow trout in 30% effluent is severely reduced and is still reduced at 10% refinery effluent. Stubblefield (1989) looked at the affects of pre-exposure to refinery effluent on rainbow trout. There was no increase in tolerance, in fact pre-exposure caused the fish to become more sensitive to the effluent at lethal concentrations. Graham and Dorris (1968) observed the behavioural effects of refinery effluent on fathead minnows. When in contact with the effluent the fish showed signs of distress, they did not school, had a sluggish or no response to disturbance. Erratic swimming, darkening of the integument, paralytic spasms and periods of immobility indicated serve stress, after which death usually followed within a few hours.

The impact of the components of refinery wastes on fish has been determined by Pickering and Henderson (1966) who recorded the acute toxicity of several petrochemical compounds to four species of fish, bluegills were the most sensitive followed by fathead minnows, goldfish and guppies. Of the compounds that were tested *O*-chlorophenol and *O*-cresol were the most toxic and methyl methacrylate and isoprene were the least toxic. Three of the petrochemical toxicities were affected by water quality. Soft water increased the toxicity of methyl methacrylate, styrene and vinyl acetate. Tests using fathead minnow fry and adults showed that the fry were more tolerant to methyl acethacrylate and less tolerant to vinyl acetate than the adults. Stubblefield (1989) used rainbow trout to determine the effects of acclimation on the toxicity of zinc, cadmium and phenol. With both heavy metals, an increase in tolerance and resistance after pre-exposure was seen in both adult and juveniles. The adults were more sensitive to the toxic effects of the heavy metals than the juveniles. There was however no change in the tolerance of the fish to phenol with pre-exposure.

4. Field surveys

Many ecological monitoring programmes have been undertaken in areas near to oil refineries to assess the impact they have on the environment. The majority of the surveys have looked at the impact on the estuarine or marine environment especially refineries that discharge onto intertidal areas. Most of these intertidal areas are mudflats or soft bottomed sandy areas although rocky shores and saltmarshes are also found. The main community that is studied in these surveys is that of the macrobenthos, as they are relatively easy to sample.

4.1. The effect on the environment

The areas around oil refinery outfalls all show a similar response to the refinery effluent, whether it is a rocky shore, soft sediment or the water column. The area around the discharge is often found to have a low diversity and abundance of fauna due to the inability of many species to survive in such close proximity to the effluent (Wharfe, 1975; Monk et al., 1979; Petpiroon and Dicks, 1982; Saha and Konar, 1984a; Mohd-Long, 1987; Moore et al., 1987; Talsi, 1987; Dicks and Levell, 1989; McLusky and Martins, 1998). In some cases the area adjacent to the outfall can be completely absent of any fauna, such as in the Hooghly Estuary, India, where no bottom fauna was found around the refinery outfall (Saha and Konar, 1984a). There are a few cases where no effect was detected in an area close to an effluent discharge (Monk et al., 1979).

Often the impacted area is limited to a specific distance from the discharge point. This distance varies depending on the site and the effluent. In Milford Haven the impacted area was limited to 200 m from the outfall (Petpiroon and Dicks, 1982), in Bahrain to 500 m (Al-Alawi, personal communication), whereas in the Hoogly Estuary it extended to 700 m (Saha and Konar, 1984a). Wharfe (1975) noted that the impacted area in the Medway Estuary was limited to an area of 1.5 km around the outfall.

In Southampton Water two distinct groups could be defined based on the level of impact. Group 1, the area of gross pollution, included the stations around the discharge that had elevated hydrocarbon and trace metals. This group was dominated by the polychaetes *Hediste diversicolor*, *Capitella capitata*, *Polydora* sp. Group 2 which was situated above and below the affected zone had more diverse fauna. The larvae of the species that were found only in group 2 were not able to survive settlement at group 1 sites, possibly due to a toxicity effect of the sediment in that area (Houston et al., 1983). McLusky (1982) investigated the spatial distribution of the benthic community of the Kinneil mudflat in the Forth Estuary, Scotland (Fig. 2). The two effluent outfalls at Kinneil also produced a similar pattern, and four zones of pollution were observed. Gross pollution occurred within 250 m of the outfall, where there was no fauna found. Between 250 and 500 m from the outfall (severe pollution) the community was characterised as having a low abundance, species diversity and biomass. Between 0.5 and 1.5 km (pollution) the fauna had a high abundance and biomass but still a relatively low diversity. Lastly the zone furthest away from the effluent (1.5–2.25 km) was described as moderate pollution and recovery. This zone had a higher diversity and a lower abundance that the previous zone. McLusky (1982) also considered the changes in the species within these areas. In the area of severe pollution only the two opportunistic species (*Manayunkia aestuarina*and *Oligochaetes*) were abundant and *Hydrobia ulvae*, *Macoma balthica* and *Nereis diversicolor* were present in low numbers. The Spionids were found in the 0.5–1.5 km zone and *Corophium volutator* and *Cerastoderma edule* were only found after 1.5 km from the discharge.

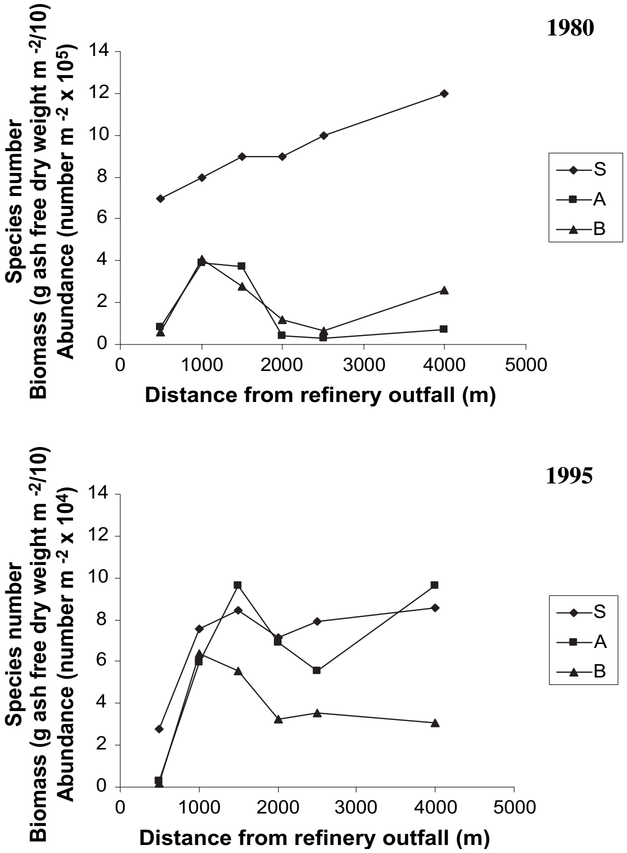

Fig. 2. Mean number of species per station (S), abundance (A) (1980: number $m^{-2} \times 10^5$), (1995: number $m^{-2} \times 10^4$), biomass (B) (g ash free dry weight $m^{-2}/10$), all expressed as the mean numbers per 500 m distance as measured from the BP refinery (Grangemouth) outfall in 1980 (upper) and 1995 (lower). Adapted from McLusky (1982); McLusky and Martins (1998).

The species that are found close to the refinery outfalls are mainly opportunistic species (Monk et al., 1979; Gibbons, 1991; McLusky and Martins, 1998) and are typical species found in organically enriched areas. Often the abundance/biomass distribution reflects the typical species abundance biomass (SAB) relationship (Fig. 2) which was proposed by Pearson and Rosenberg (1978) for organic enrichment. Scott (personal communication) discovered that the Kinneil mudflat on the Forth estuary had a higher biomass of *Oligochaetes* and *Nereis diversicolor* than other similar mudflats in the estuary. There is also some evidence to suggest that refinery effluent may reduce the growth of some species. Yule (personal communication) found that close to the refinery effluent discharge *Macoma balthica* and *Hydrobia ulvae* were smaller than those from further away.

Effects on the flora have also been seen. In both the Medway Estuary and Milford Haven, algal growth has been seen to increase near the effluent, algae are notably abundant around the outfalls in these areas (Baker, 1976; Petpiroon and Dicks, 1982). Often oil is thought to be the main component of the effluent to cause the adverse effects as it is thought to be toxic. Baker (1971) deduced that the reason for the death of *Spartina* and the appearance of bare patches of mud was repeated light oiling of the *Spartina* shoots. The oil content of the soil, the pH of the water and soil the sulphide concentration and temperature of the effluent did not seem to have an effect and *Spartina* was found to grow in jars of outfall water and pots of soil from the denuded area. Studies of the macrophytes in experimental wetlands have shown that petrochemical effluent was not the limiting factor for the growth of three species (*Scirpus californicus, Typha subulata*and *Zizaniopsis bonariensis*) and that water and/or nutrients had a greater effect (Campagna and Marques, 2001).

Some field studies however suggest that it may be other components within the effluent that could be causing the effects. Wharfe (1975) found that the species numbers negatively correlated with the oil concentration of the sediment but *Nereis diversicolor* was present in areas contaminated with oil. Therefore it was concluded that oil alone could not be responsible for the effects seen in the area around BP Colemouth Creek. The oil content of the refinery effluent at Milford Haven was reduced but no reduction in the area of impact was seen. It was considered that the low salinity of the effluent might be an important factor for causing the impact to this area rather than the oil (Petpiroon and Dicks, 1982).

4.2. Recovery

It can be seen that if the toxicity of the effluent is reduced or the effluent is stopped completely that the area of impact is able to recover. The time it takes for the area to recover varies and depends on the area and the type of organisms involved. In Porvoo, Finland, the subtidal area was monitored to observe the effects of the addition of a new treatment plant to the oil refinery there in 1973 (Leppakoski and Lindstrom, 1978). An improvement in the macrofauna was seen in 1974 and 1975 with an increase in the number of species and diversity. The species that were found to recolonise most successfully included the amphipods *Pontoporeia affinis* and *Corophium volutator*, the Oligochaete *Tubifex costatus*, the polychaetes *Harmathoe sarsi* and *Polydora redeki* and the bivalve *Cerastoderma edule*.

The addition of a biological treatment system to oil refineries in both the Forth estuary, Scotland and the Peace river, Canada caused a decrease in the opportunistic species and again allowed the less tolerant species to recolonise (Gibbons, 1991). The size of the area of enrichment gradually decreased over time (McLusky and Martins, 1998; Fig. 2) and recent unpublished studies of the area have shown that the area affected by the petrochemical discharges has now disappeared completely. The improvement in the quality of the effluent at an oil refinery in Southampton water in 1971 produced a dramatic improvement in the condition of the nearby saltmarsh (Dicks, 1976; Dicks and Levell, 1989).

The oil refinery at Milford Haven closed in March 1983 and monitoring of the rocky shore area was carried out to see if there was any change (Dicks and Levell, 1989). The year 1984 saw increased recruitment of juvenile limpets all along the shore but especially near the outfall. During the following years further recruitment was noted, the average limpet became smaller but where found at increased densities. The barnacle population showed a different pattern. In 1984 there was an increase in the numbers of juvenile and adult barnacles but not near the outfall where there were fewer still. In 1985 a distinct gradient of density could be seen with increased densities going away from the outfall, however in 1986 this gradient was less pronounced and only one station near to the old outfall had reduced numbers of barnacles. Therefore it was concluded that the effluent had been the main factor causing the exclusion of limpets and barnacles from the area around the outfall.

5. Conclusions

The main implication from the studies on the effects of refinery effluents is that generalisations cannot be made. Each refinery is made up of different plants, which produce different effluents that can vary from day to day. The fate of the effluent is dependent on environmental conditions, i.e. weather and the recipient. Volatile compounds are lost from the effluent into the atmosphere where as the majority of the non-volatile compounds, like the hydrocarbons, end up in the sediment. Sediment analysis for hydrocarbon concentrations can be useful in determining the history of the input into that area.

Toxicity tests are very useful indicators of the possible impacts that refinery effluents may have on aquatic organisms. Lethal tests are good for indicating the relative toxicities of different chemicals and the differences between different species. Whereas sublethal tests are more realistic in that they consider the impacts on communities, not just to the individual, but to the population through effects to the reproductive success and growth.

The tests have shown that refinery effluent is toxic at different concentrations to algae, invertebrates and fish. Marine/estuarine species are more sensitive than freshwater species and larvae tend to be more sensitive than adults are. Crustaceans seem to be the most sensitive of the invertebrates that have been tested. The conditions of the tests have also shown that for marine/estuarine species, decreased salinity and increased temperature can increase the toxicity of certain chemicals. The presence of sediment in some cases seems to reduce the toxicity but in other cases has been shown to increase the toxicity of the chemicals. The chemicals that have been identified as being the most likely cause of the toxicity are the PAHs, but also ammonia and sulphides have also shown highly toxic effects. Sublethal tests have shown that genetic mutations can occur in the offspring of fish kept in effluent. Reproductive success and growth is reduced in the presence of effluent and its components.

Field surveys have found that effluents have an impact on growth, as organisms that live close to outfalls are often smaller than others further away are. The majority of studies have shown that there is a toxic effect from the effluent, which can be seen as an impoverished area around the refinery discharge. In this area there is either no fauna or a select fauna of pollution tolerant species at low densities. The size of this impact area is variable and is probably dependent on the effluent and the site of the outfall. The invertebrate density is usually found to increase with distance from the outfall. There is often also an enrichment effect, which can be seen as a peak in biomass or abundance. Often the high biomass is due to one species and is often near to the impoverished area. This conforms to the typical species, abundance and biomass (SAB) relationship where there is a peak of opportunistic species within a few hundred metres of the source (Pearson and Rosenberg, 1978).

Refinery effluent has also been attributed as the cause of lack in recruitment in some areas, that it may either kill young settlers or may deter them from settling near discharges. Algae have been seen to be growing in areas near effluent outfalls and are thought to be fairly resistant due to their mucilage covering. Field surveys have also observed the effects on the community in areas where the refinery effluent has been stopped. In all cases the clear recovery of the impacted area was observed. The time taken for the area to recover varied and is probably dependent on the extent of the impact from the effluent and the community under consideration.

It is therefore possible to detect two effects that oil refinery effluent has on the environment. Firstly it has a toxic effect close to the outfall, which is seen by the absence of all or most species. Secondly there is an enrichment effect which can be distinguished as a peak in the abundance or biomass. Unfortunately both these effects are not exclusive to oil refinery pollution. The oil and other organic chemicals such as ammonia in the refinery effluent cause the organic enrichment effect. The same effects are seen with other organic effluents like sewage waste. The toxicity effect is caused by high concentrations of organic compounds and/or high concentrations of the inorganic compounds such as phenol in the refinery wastes. The same effects are also seen with other chemical wastes, detergents and sewage pollution. It is therefore very difficult in areas where there are other sources of pollution to determine exactly which pollution source is causing the observed effects.

It therefore seems that when considering the possible impacts from refinery and petrochemical effluents each case must be considered separately. It is likely that the area will be impacted but to what extent depends on the receiving water and any other pollution sources in the area. Off-shore discharges will have less effect than a shore discharge and poor dispersion will intensify the problem (Baker, 1976). The installation of new treatment process has been seen to reduce the impact of the effluent. This means that the impact from refinery effluents is diminishing as the number of refineries that have effluent treatment processes is increasing.

Most of the literature that is readily available on the effects of oil refinery effluents is from the UK and Europe. One of the major problems in this area of research is that although monitoring of areas affected by refinery effluents is being carried out, the majority is performed by industry and the reports may not be widely available. There is clear evidence however (Concawe, 2004) that the quantities and toxicity of refinery effluents has shown a drastic reduction in the past two decades. As a result the previously impacted areas in many estuaries and coastal environments can and do show effective recovery.

There are several areas that still need further investigation. The effects of refinery effluent on algae has not been extensively studied as well as the effects on the Meiobenthos. There have been many studies concerned with the lethal toxicity of refinery effluent but relatively few considering the sublethal effects, especially to algae and invertebrates. This is an area that needs more attention especially as the refinery effluents are generally now much cleaner and are more likely to be having sublethal rather than lethal effects. Field studies may also need to consider sublethal effects as very few have considered the effects on growth and the recruitment of aquatic organisms.

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