ENVIRONMENTAL IMPACT OF USED MOTOR OIL

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(Received May 11th, 1988; accepted July 19th, 1988)

ABSTRACT

The information concerning the effects of used motor oil on the environment is reviewed. The production and fate of used motor oil are analyzed and the effects on soil and aquatic organisms are described. The combustion of waste crankcase oil, with particular reference to environmental impact, is discussed. The mutagenic and carcinogenic effects of used motor oil are described. Information on the biodegradation of lubricating motor oil is also reviewed.

The available information shows that used motor oil is a very dangerous polluting product. As a consequence of its chemical composition, world-wide dispersion and effects on the environment, used motor oil must be considered a serious environmental problem.

INTRODUCTION

Used motor oil is a very dangerous polluting product. It contains polynuclear aromatic hydrocarbons (PAH) and high levels of heavy metals. PAH, such as benzo[a]pyrene, are well known for their high carcinogenicity. Considerable quantities of heavy metals, such as Pb, Zn, Cu, Cr, Ni and Cd, are contained in used crankcase oil; these metals are highly toxic to organisms.

Chronic pollution due to used motor oil reaches several millions of tons yearly. In contrast to petroleum pollution, used motor oil pollution is worldwide because the major sources are automotive traffic and industrial activity. Moreover, apart from hydrocarbons and heavy metals used crankcase oil contains other compounds that are dangerous to the environment, such as lubrication additives. Motor oil pollution can damage the soil and the aquatic environments, as well as the atmosphere when waste oil is burned. These are the reasons why it is necessary to consider used motor oil pollution and petroleum pollution separately. The massive crude-oil pollution of the sea has resulted in extensive research on hydrocarbon biodegradation and effects on the environment, which have been reviewed many times. However, pollution due to used motor oil has not received the same attention. The purpose of this review is to gain an insight into the production and fate of used crankcase oil; the effects of dispersion and spillage of used motor oil on the soil and aquatic environment; and the environmental importance of waste oil combustion. Finally, the toxic, mutagenic and carcinogenic properties of used motor oil are considered.

PRODUCTION AND CONSUMPTION OF LUBRICATING OILS

After the petroleum refining processes, several products, mainly fuels and lubricating base oils, are obtained. This work reviews the literature on lubricating motor oils and their impact on the environment.

Apart from engine oils, there are many other lubricating oils: industrial transmission oils, hydraulic oils, heat-treatment oils, heat-transfer oils, cutting oils, electrical oils, rolling oils, food-machinery lubricating oils, etc. Since 1930 almost all of the lubricating oils have been obtained from petroleum.

The lubricating base oils from the refinery processes of crude oil are very complex mixtures of hydrocarbons: linear and branched paraffins; and cyclic alkanes and aromatic hydrocarbons (> C_{15} with boiling points between 300 and 600°C. However, lubricating oils obtained from the residual fractions have some compounds with boiling points of up to 815°C. The technology used in the fabrication of the different lubricating oils is specific for each commercial company. Moreover, the type and quantity of additives are determined by future utilization and by commercial patent. The normal production processes of lubricating base oils, after the refining processes, are: propane desasphalting; solvent extraction; hydrotreating; solvent dewaxing; acid treating and finishing.

The world production of lubricating oils is almost 1-2% of refined crude oil [1,2], and world consumption (excluding Eastern Europe and China) was 23.8 million tonnes in 1980 [3]. A good contemporary estimate of world consumption is 35–38 million tonnes of lubricating oil yearly [4]. The distribution of lubricating oils according to utilization is nearly the same in all of the industrialized countries, with almost one-half consumed by industry and the other half by automotive transport [5]. The relationship between industrial activity and industrial consumption of lubricating oils is so close that industrial consumption can be used as an indicator of industrial activity [6]. In the case of automotive oils, the situation is more confused. The number of automotive vehicles is increasing constantly and the consumption of crankcase oil is also increasing, but not in the same proportion. This is due mainly to the reduction of unitary oil consumption. For example, in Europe, the annual consumption of crankcase oil per car was 21.2 kg of oil in 1975, and in 1985 this consumption was only 12.5 kg [6]. This decrease can be considered a consequence of the progress in motor technology and oil technology (refining and additives), which has lengthened the time between oil changes and has decreased leakage and losses by combustion when the motor is running. This reduction in motor oil consumption for vehicles has been observed since the 1950s [7].

PRODUCTION AND FATE OF USED LUBRICATING OIL

The production of used crankcase oil is estimated to be between 65 and 68% of the sales of new motor oil; one-third of the oil consumed by motors is lost when the machine is running [8,9]. In the case of industrial oils, the production of used oil represents 30–57% of consumption [2, 10].

The losses of oil when the motor is running comprise between 0.5 and $2.0 \text{ g h.p.}^{-1} \text{ h}^{-1}$, which is equivalent to 1.5 or 2.5% of fuel consumption. A four cylinder car of between 1 and 1.51 capacity losses from 0.2 to 0.31 of lubricating oil for each 1000 km of roadway. These losses are not always so small, a level of 0.5–1.01 per 1000 km being more usual [7]. In diesel engines with 9 or 10 cylinders, the oil losses are between 0.5 and 23 g h⁻¹ according to the loading and the rotation speed [11]. The lubricating oil can be lost in two ways: (a) by escaping through joints, as well as through the breather valve, the dipstick hole and the oil filter, or due to the recycling of vapours and oil in the PVC systems, etc. (b) by oil passing between piston and cylinders or between valve stems and guides. In this case, the oil passer to the combustion chamber and the losses can represent as much as 90% of the total oil loss, but more commonly probably 50%. Several factors determine the level of oil loss during engine operation: volatility and viscosity of the motor oil; mechanical condition of the engine; speed; and the driver [7].

The production of waste crankcase oil in the U.S.A. was estimated at more than 9 million tonnes in 1980 [9]. The world production of used motor oil can be estimated at almost 25–28 million tonnes in addition to 12–15 million tonnes lost yearly during engine operation.

At present, used motor oil has many fates: as auxiliary fuel; for re-refining; as road oil or incorporated into asphalt; disposed of in landfill; and unknown fates. For example, in the U.S.A. the estimate is as follows: 31.7–50.0% of used motor oil is utilized as fuel; 11.0–16.7% is incorporated into asphalt for roads; only 3.3–9.2% is re-refined; and, finally, 23.0–30.0% of waste motor oil produced is directly disposed of into the environment [2,8,10,12,13].

COMPOSITION OF USED MOTOR OIL

The chemical composition of lubricating oils, as with all other petroleum products, varies with the crude-oil source, the refining process and the additives present. The fabrication process of lubricating oil has changed significantly in recent years in order to eliminate undesirable compounds, such as polyaromatic hydrocarbons (PAH). For this reason, two-thirds of the base oil produced in industrialized countreles is solvent-refined.

Generally, aliphatic compounds represent between 73 and 80% of the total weight of the oil. This fraction is composed of alkanes and cycloalkanes of 1–6 rings. Monoaromatic hydrocarbons make up 11–15% of the weight, diaromatics 2–5% and polyaromatic and polar fractions 4–8% [14]. The polar fraction is made up of aromatic compounds which contain sulphur, nitrogen or oxygen. In certain cases, probably when the oil has not been refined very well, the

TABLE 1

Functional types of lubricating oil additives

Chemical modifiers	Physical modifiers
Boundary lubrication additives:	Viscosity modifiers:
Wear inhibitors	Viscosity index improvers
Friction modifiers	Thickeners
Lubricity agents	Pour point depressants
Extreme pressure agents	Emulsion modifiers
Corrosion inhibitors	Foam decomposers
Oxidation inhibitors	Tackiness agents
Detergents and dispersants	Dyes

aromatic compounds can represent 37-50% of the oil [15,16]. The fraction of aromatic hydrocarbons is composed of compounds with 1-5 aromatic rings.

Before discussing the relationship between oil composition and use, it is important to mention that lubricating oils are characterized by their high additive content. During oil fabrication, and in order to improve its physical and chemical properties, several types of additive are employed. The different types of additive are summarized in Table 1. The additive content of lubricating oils can be as much as 20%, the most important being detergents and dispersants at 2–15% of the weight of the oil. Of the oil additives, several compounds are known to be dangerous environmental contaminants. Zinc diaryl or dialkyl dithiophosphates; molybdenum disulphide; zinc dithiophosphate; heavy-metal soaps and other organometallic compounds which contain heavy metals [1,17,18]. That is why the zinc content of new motor oil is high; new motor oil contains ~ 1500 μ g g⁻¹ of zinc and 87 μ g kg⁻¹ of cadmium [19].

During motor operation, lubricating oil is chemically transformed by oxidation, nitration, cracking of polymers, decomposition of organometallic compounds, etc. This change is due to the high temperature and the high mechanic strains that the oil is subjected to during motor operation [20]. On the other hand, motor oil accumulates different contaminants, such as fuel (petrol or diesel), water, antifreeze and insoluble particles. These particles principally originate from atmospheric dust, metals, metal oxides and combustion products. The water content can be as much as 9%, fuels can represent up to 10% and solid particles up to 8% [1]. The nitrogen content of used motor oil is generally 0.05–0.18%, sulphur content 0.22–0.55%, phosphorus content 80–32 000 μ g g⁻¹ and chloride content ~ 3500 μ g g⁻¹[9,14,21].

One of the more important differences between new and used motor oil is the heavy metal content. The metal content of used motor oil is very important, because many of these metals are potentially very dangerous to living organisms. These metals originate from the fuel and from motor wear. Used motor oil contains high concentrations of Pb, Zn, Ca, Ba and Mg, and lower concentrations of Fe, Na, Cu, Al, Cr, Mn, K, Ni, Sn, Si, B and Mo [9,14,19,21,22]. The concentration of metals in lubricating oil increase with motor operating

TABLE 2

Metal	Used motor	oil from					
Gasoline		Diesel	Local gasoline station			30 used oil samples ^e	
	engine ^a	engine [*]	b	с	d	Average	Max.
Pb	7500	75	1075.0	3091.5	3950	7097.0	13885
Zn	1500	1300	265.0	1128.5	740	1061.0	2500
Cu	17	18	27.5	6.0	40	28.0	56
Cr	21	3	BLD	1.0	ND	10.5	24
Ni	BLD	BLD	8.5	0.6	ND	1.2	5
Cd	ND	ND	0.1	0.5	ND	ND	ND

Concentration $(\mu g g^{-1})$ of heavy metals in used motor oils

^aRaymond et al. [22]. ^bMumford et al. [21]. ^cVazquez-Duhalt and Greppin [19]. ^dBecker and Comeford [9]. ^eCotton et al. [14]. ND, not determined; BLD, below limit of detection.

time and the amount is dependent on fuel type and the mechanical condition of the engine. The heavy metals in used motor oil can amount to $(\mu g g^{-1})$ (Table 2): Pb, > 13000; Zn, 2500; Cu, 50; Cr, 20; Ni, 5; and Cd, 0.1. The lead content has been reported to be as high as $45\,000\,\mu g g^{-1}$ or 4.5% [23]. Other metals that can be present in significant amounts are, for example, Ca, $4000\,\mu g g^{-1}$; Mg, $1000\,\mu g g^{-1}$; and Na, $600\,\mu g g^{-1}$.

Other types of compound present in used motor oil are polyaromatic hydrocarbons (PAH), which are very dangerous to health because some are known to be mutagenic and carcinogenic [24]. The PAH content of new moitor oil is relatively low [25], but increases with motor operating time. In this way, the PAH content of used motor oil is higher than that of new motor oil. Used oils can contain 670 times more PAH than new motor oils [26]. This increase varies according to engine type. For example, the PAH content of used crankcase oil from the Diesel motors of lorries can be three times higher than that of new oil; for diesel buses it can be six times higher than that of new oil; and for diesel cars it can be 30 times higher than that of new oil. The PAH content of used motor oil from petrol motors can be 180 times higher than that of new crankcase oil (Table 3) [25,27-29]. The benzo[a] pyrene content of new motor oil can be up to $0.266 \,\mu g \, g^{-1}$, but that of used motor oil from petrol cars can be up to 216.8 μ g g⁻¹ [30]. This means that the concentration of benzo[a]pyrene in used crankcase oil can be 1000 times higher than that in new oils. This difference is due to the accumulation of petrol PAH in the motor oil during engine operation. This accumulation can be up to 93% of the PAH content of the petrol and only a small amount of PAH is emitted with the exhaust gas. PAH are also formed during motor operation. The PAH emissions in the exhaust gas do not depend on the PAH concentration in the Petrol, but the amount of PAH accumulated in the motor oil is directly correlated with its concentration in the petrol. This accumulation also depends on the motor-starter type [31].

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PAH	

Polycyclic aromatic	Concentration (µg	g ⁻¹)			
пуагосагооп	New motor oil	Used motor oil from petrol vehicles	Used motor oil from diesel vehicles	Used motor oil from diesel lorries	Used motor oil from diesel buses
Anthracene	0.002-0.030	1.6-10.8	0.5-4.4	0.02-0.12	0.03-0.16
Benzo[a]pyrene	0.008 - 0.266	5.2 35.1	0.7 - 11.9	0.13 - 0.60	0.07 0.55
Benzo[e]pyrene	0.030 - 0.402	6.4 - 48.9	1.3 10.7	0.23 - 1.10	0.29 - 1.04
Benzo[ghi]perylene	0.010 - 0.139	4.4 - 85.2	2.1 - 16.0	0.20 - 0.78	0.26 - 0.65
Benzo[b]naphtho[2,1-d]thohene	0.097 - 9.430	ND	0.7 - 4.3	0.78 - 6.20	1.60 - 4.80
Benzofluoranthenes $[b + k + k]$	0.013 - 0.234	5.7 - 44.3	1.8 - 16.8	$0.26 \cdot 1.30$	0.37 - 1.20
Chrysene + triphenylene	0.182 - 11.900	8.7 - 74.0	5.1 - 42.8	1.60 - 6.10	1.90 - 8.00
Coronene	0.001 - 0.016	2.8 - 29.4	0.1 - 6.4	0.10 - 0.13	0.00 -0.08
Fluoranthene	0.008 - 2.750	3.4 - 109.0	1.3 - 58.9	0.18 - 2.90	0.40 - 2.70
Indeno[1,2,3-cd]pyrene	0.001 - 0.020	2.1 - 12.5	0.8-9.0	0.06 - 0.28	0.07 - 0.25
Perylene	0.007 - 0.224	1.9 - 10.0	0.4 - 2.7	0.11 - 0.35	0.04 - 0.29
Pyrene	0.039 - 6.530	5.7 - 326.0	1.4 - 78.0	0.33 - 6.40	0.90 - 4.90

^a Grimmer et al. [25,27,28]. ND, not determined.

SPILLAGE OF USED MOTOR OIL INTO SOIL

Used oil can be dispersed into the soil in four different ways: escape and loss of oil during motor operation; during application on rural roads for dust control; during asphalting with asphalt-containing waste crankcase oil; and, finally, when it is placed directly in a landfill. Here, the consequences of the used lubricating oil on the soil environment are analyzed.

One-third of the lubricating oil sold is lost during use; some is lost on the pavement surface, in the streets, roads and in car parks. The oil remains on these surfaces until stormwater or the municipal services wash the oil off, when it is transported by waste pipe in the case of urban zones, or transported to adjacent soils in the case of roads.

As is well known, dust [32] and runoff water [33–36] from streets and roads have a high content of heavy metals and other pollutants. The origins of metals present in the runoff water from roads and streets are very varied (atmospheric dust, automobile traffic, building corrosion, etc.), but the contribution of automobile traffic is very important. The heavy metal content of soils and plants around the roads is inversely correlated with distance from the road and with depth [37,38]. The metal emissions from vehicle exhaust gas are very important, but the contribution of used motor oil cannot be dismissed. The importance of the contribution of used crankcase oil can be corroborated by the fact that the PAH content of runoff is ~ 20–200 μ g l⁻¹ in automobile traffic zones, and only 0.2–4 μ g l⁻¹ in residential zones [34]. Moreover, a direct correlation has been detected between heavy metal and hydrocarbon contents of stormwater runoff from a main road [39].

The hydrocarbon content of runoff water from roads can be > 10 mg l⁻¹, as opposed to 0.9 mg l⁻¹ in domestic wastewater. The hydrocarbon concentrations determined during five storms were between 2.81 and 5.30 mg l^{-2} , with an average of 3.69 mg l^{-1} . The hydrocarbon composition of the water was 70% aliphatic and 30% aromatic, which is very close to the composition of the motor oil utilized in the locality. The origin of the hydrocarbons could be confirmed by the hydrocarbon distribution (C₁₅-C₄₀) and by the gas chromatographic profiles, which were very similar to those of the motor oil. Of the total hydrocarbons from stormwater on roads, 86.4% was associated with particulate matter [40]. UV-fluorescence spectroscopic analysis of hydrocarbons carried by New york effluent to the sea showed that most came from used crankcase oil [8].

The disposal of waste oils in landfills represents 30% of the total used oils in the U.S.A.; in other countries the used oils are also disposed of in this way [13]. Depending on the porosity of the subsoil, 5–401 of oil can remain in each cubic metre of soil. The saturation concentration of oil in groundwater varies between 5 and 300 mg l^{-1} , depending on the mineral soil [41].

After an indeterminate number of years, the oil residue on two rural roads on which used motor oil had been applied for dust control was analysed. Approximately 1% of the total oil applied $(21m^{-2})$ remained in the top 3 cm of the soil. The oil concentrations in the soil up to 3 cm deep were between 0.13 and 13.4 g kg^{-1} of soil, and the oil penetration below the top 3 cm was negligible [42].

The incorporation of used oil into asphalt, as road oil, accounts for 15% of the total used oil in the U.S.A. This oil can be immobilized forever, but as well as the losses during the first days after application of the asphalt, there is also surface erosion. The use of chains on tyres and nailed tyres during the winter accelerate the rate of road and street erosion. The wear of streets in Germany has been estimated at 0.8-1.0 mm each year, but the extent of wear depends on several factors: asphalt quality; traffic density; the season and climate; location (acceleration or braking zone); and also if the street or road is dry, wet or laden with snow. In Germany, the wear of streets has been estimated at 0.1-1.0 mm during the summer and 0.5-6.7 mm during the winter [43].

A primary effect of the dispersion of used motor oil in the soil is a very important change in the amount and species of microorganisms. The application of hydrocarbons in the soil promotes an increase in microorganisms able to biodegrade these substrates. A very interesting study of used motor oil biodegradation in different soils [22] has shown that such changes in the soil microorganisms occur when a hydrocarbon mixture is applied. An increase in the population of specific hydrocarbon-biodegrading microorganisms was evident a year after application.

The spillage of petroleum on soil produces some important changes in the microorganism communities that participate in the nitrogen cycle, as well as in the metabolic activity of the aerobic microorganisms able to oxidize hydrocarbons. The petroleum fills the pores between the soil particles and hampers oxygen access. A significant number of microzones arise, in the soil aggregates, which have an oxygen deficiency. Another factor that promotes the development of anaerobic microzones in the contaminated soil is the development of aerobic hydrocarbon-oxidizing microorganisms. The numbers of nitrogenfixing, denitrifying and ammonifying microorganisms in the contaminated soil are greater than in the uncontaminated soil [44]. The increase in the soil of the content of easily accessible substances, arising from aerobic hydrocarbon biodegradation, stimulates an increase in the numbers of anaerobic nitrogenfixing microorganisms, such as Clostridium. Because of this the nitrogen content of the contaminated soil is greater than that of the uncontaminated soil. Denitrifying microorganism numbers are also increased by the presence of hydrocarbons. This type of microorganism is stimulated by the increase in organic substrates and the low oxidation-reduction potential. This increase has no effect on the intensity of the denitrifying process, which is the same in the contaminated and uncontaminated soils. As is well known, hydrocarbon oxidation is catalysed by aerobic organisms, with the participation of oxidoreductase enzymes, and the initial oxidation requires the presence of atmospheric oxygen as an electron acceptor. Also, nitrate reductase, responsible for reducing nitrate, is activated only under anaerobic conditions and is inhibited by oxygen. This means that the diminution of nitrate reductase activity is compensated for by the increase in the quantity of denitrifying microorganisms. Finally, protease activity is also inhibited by the presence of petroleum in the soil, but this is compensated for by an increase in ammonifying microorganisms, which increase the amount of protease excreted to the environment [44]. Indeed, autoregulation of the nitrogen cycle due to the presence of hydrocarbons reduces the effects of pollution in this cycle, but there is no evidence that this occurs in other biological cycles in the soil.

It is known that the presence of heavy metals in used motor oil can strongly inhibit primary production, carbon mineralization, nitrogen transformations and mineralization of sulphur and phosphorus [45]. In the case of used motor oil, the presence of lead can diminish hydrocarbon biodegradation, as has been shown to occur when lead has been added to contaminated soils in petroleum [46]. Used motor oil and the lead contained in this oil remain in the first 20 cm of soil for a year after the spillage, i.e. it remains at a depth where most microbial activity take place [22].

The nematode concentration in the soil is decreased strongly for a long period by the application of used oils from diesel and petrol engines. The growth of plants (turnips and beans) has been shown to be inhibited in soils contaminated with used motor oil, and the lead concentrations in surviving turnips and beans were, respectively, 450 and 150% greater than those grown in uncontaminated soil [22]. As mentioned previously, motor oil contribution to the pollution of roads can be very significant. The lead and zinc concentrations detected in earthworms (331.4 and 670 μ g g⁻¹, respectively) living in soil near roads are probably fatal for their predators [47].

SPILLAGE OF USED MOTOR OIL IN AQUATIC ENVIRONMENTS

As already mentioned, motor oil is generally spilled on the land but this oil can be transferred rapidly to aquatic environments by rain and runoff waters. This transfer is important in roads and streets of urban zones near lakes and seas. A Swedish study [48] showed that the hydrocarbon content of runoff water from a road was 10 mg l^{-1} and in the runoff from the streets of an urban zone was $\sim 1 \text{ mg l}^{-1}$. Another similar study in Washington Lake [49] showed that the concentration of aliphatic hydrocarbons in the runoff water from roads carrying high-density automobile traffic varies from 6 to 24 mg l^{-1} . In the same study the aliphatic hydrocarbon concentrations of runoff from residential zone streets were only between 0.2 and 7.5 mg l^{-1} . The paraffin content of hydrocarbons and the gas chromatograms support the fact that the principal source of hydrocarbons is lubricating motor oil. Pollution of the lake has caused the hydrocarbon content of the superficial sediments to increase to $1.5\,\mathrm{g\,kg^{-1}}$ (0-20 mm), which is greater than the hydrocarbon concentration in deep sediments (0.03 g kg^{-1}) from 300 mm. The increase in the hydrocarbon content of the lake sediments is correlated with the development of the Seattle metropolis [49].

The origin of most hydrocarbons in runoff waters is doubtless the lubricating motor oil from automobile traffic. This can be corroborated by the results obtained in a hydrocarbon analysis of runoff waters from several storms, where the hydrocarbon contents were $2.18-5.30 \text{ mg l}^{-1}$, with an average of 3.69 mg l^{-1} [40]. In this study the composition of hydrocarbons from road drainage was similar to that of lubricating motor oil. The proportions of aliphatic and aromatic hydrocarbons (66 and 33%, respectively), the chain length ($C_{15}-C_{40}$) and the gas chromatograms were very similar for the hydrocarbons obtained from the runoff samples and those from crankcase oil.

In urban wastewater arriving at a treatment station, the hydrocarbons are the organic compounds with the most resistance to the biodegradation process, in comparison with the other organic substances currently present [50]. Effluent samples from the outlet of wastewater treatment stations of New York bay contained up to 40 mg l^{-1} hydrocarbons, and in consequence the hydrocarbon concentration in the surface water of the bay was up to ten times greater than the normal concentration in seawater. The hydrocarbon concentration in New York bay is $10-20 \,\mu \text{g} \, \text{l}^{-1}$, whereas the normal concentration in seawater is $\sim 2 \,\mu \text{g} \, \text{l}^{-1}$. Gas chromatographic and UV spectrophotometric analysis has shown that the hydrocarbons probably originate from used lubricating oil from automobile traffic [8].

Oil losses during engine operation are not the only source of contamination by used motor oil. Roads oiled with crankcase oils for dust control can also be an important source of water contamination. For example, in one study two oil patches were noticed in shallow pools on the banks of a stream. The oil patches were produced by an oiled road and the oil was deposited during a period of high stream flow [42]. The oil incorporated into asphalt can be mobilized by stormwater after the application of the asphalt. Hydraulic oil has been detected in industrial cooling water at levels of up to 65 mg l^{-1} [51]. Finally, outboard two-stroke motors are an important source of motor oil contamination of freshwater environments [52], and navigation accidents can result in the spillage of thousands of litres of lubricating motor oil [53].

The primary effect of the presence of hydrocarbons in aquatic environments is doubtless a change, as in soil pollution, in the composition of microorganism communities [54]. Although the effect can be an increase in the number of total microorganisms able to biodegrade the hydrocarbons [55], usually the microorganisms are strongly inhibited. The toxicity of several petroleum products to different microbial species in sea and freshwater environments has been studied [56-58]. Generally, hydrocarbons in an aquatic environment provoke an increase in yeast and bacteria and able to degrade this substrate, and a diminution of other microorganisms which are pollution-sensitive, principally phytoplankton species. Petroleum hydrocarbons [59-66] and those from shale oil [67-69] inhibit the growth, photosynthetic activity and respiration of algae. At low concentrations, the presence of certain hydrocarbons can stimulate microalgal growth, but an increase of hydrocarbon concentration in the medium tends to inhibit phytoplankton activity. Obviously, several physicochemical factors determine the effect of hydrocarbons on algae. In the same way, the presence of bacteria able to degrade hydrocarbons can diminish the toxic effect of hydrocarbons on photosynthetic microorganisms [70,71]. The

photosynthetic rates of phytoplanktonic microorganisms can be depressed severely by the effect of outboard-motor fuel oil. The results indicate that this oil tends to have a marked inhibitory effect on the photosynthesis of phytoplankton communities as a whole, while individual species may not be affected [72].

The damage to crustaceans, molluscs and fish caused by hydrocarbon pollution can also be very important [73–75]. Motor oil from outboard motors has caused significant damage in shellfish [76]. It has been found that used motor oil is one of the most important mutagenic agents in the aquatic environment [29,77–80].

BURNING OF USED MOTOR OIL

Most used motor oil is employed as an auxiliary fuel, sometimes in special burners for this type of waste in connection with gas-cleaning systems. Unfortunately, such burning is mainly carried out in inadequate installations The heat of combustion of waste crankcase oil is ~ 12240 kcal kg⁻¹ [9,81], which is the same as the heat of combustion of petroleum-derived fuels, but it is much less expensive.

As shown previously, used motor oil accumulates high quantities of heavy metals, and exhaust gas from the combustion of waste oil also contains high levels of heavy metals. Although most of the metals remain in the ash residue, which can contain up to 8% Pb and 7.2% Zn, lead emissions can represent up to 70% of the total lead introduced into the burner, and zinc can reach the same values. Metal emissions during the combustion of waste motor oil are different for each oil and for each burner type. One of the characteristics of all types of burner is that most metal emissions are in particle form (dust). The emission particles can contain up to 33.3% Pb, 10% Zn, 1% Cr and 0.3% Cu. Consequently, with a 0.5 μ m filter, it is possible to retain 87–93% of the Pb, 41–59% of the Zn and 22–100% of the Cd emitted. The metal emissions in gas form are not negligible and can represent 0.81–1.29% Pb and 0.23–0.29% Zn [81,82]. The amount of metal emitted from different types of burner when waste crankcase oil was burnt were as follows (in gm⁻³ of burned oil): 4793–9627 PbO; 383–695 ZnO; 31–75 Al₂O₃; 14–57 Cr₂O₃; 1–19 CuO; and 7–15 SnO [10].

In addition to heavy metals, the combustion of used motor oil produces other compounds which are also dangerous to the environment. Used motor oil contains high amounts of sulphur, nitro-compounds, solid particles and chloride. During the combustion of used oil, large quantities of toxic gases, such as SO_2 , NO_x and HCl, can be emitted. Hydrochloric acid is emitted in very high concentrations during the combustion of certain oils, such as cutting oils and metal-working oils, which can contain 5% chloride.

The toxicity of the emission particles and residue products from two different types of burners using used motor oil has been evaluated [21]. Both burners emitted fine ($\leq 3 \mu$ m), respirable particles. The emission particles can contain high concentrations of toxic heavy metals, especially lead, which was

present at concentrations as high as 7.5%. The toxicity of emission particles and waste residue was evaluated in three bioassay systems, including rabbit alveolar macrophage cytotoxicity (in vitro assay), intratracheal injection infectivity assay, and a peritoneal irritancy test in mice. The emission particles from both burners and leachate from one residue produced a dose-related reduction in viability and cellular adenosine triphosphate (ATP) in alveolar macrophages following 20-h exposure. Mortality due to infection with aerosolized Streptococcus sp. was not significantly elevated by intratracheal injection of emission particles from one burner at $100 \,\mu g$ in each mouse, whereas a similar dose of ash from the other burner produced significant elevations in mortality (61.1%). Emission particles from both burners caused a dose-related sensory irritant response when injected into mice. In comparison with other environmental particles tested, the emission particles from the combustion of waste crankcase oil were each ranked to be among the most toxic according to the percentage reduction of cellular ATP in the rabbit alveolar macrophage cytotoxicity assay and were most toxic for the mouse bacterial infectivity assay. Twenty-three other environmental particles were tested, including coal-fired power plants and fluidized bed combustors, diesel-exhaust emission particles. volcanic ash, ambient air particles, and residual oil fly-ash [21].

MUTAGENICITY, CARCINOGENICITY AND TOXICITY OF USED MOTOR OIL

Several studies have been carried out on the mutagenic and, principally, carcinogenic effects of lubricating oils [4,83]. A lot of information is available on the effects of different fractions of petroleum refining. This information includes the base lubricating oils and, specifically, several lubricating products, such as metal-treating oils, metal-cutting oils, electrical oils, etc. In this work, information concerning the toxic effects of motor oil was selected because it is the most important waste lubricating oil.

The mutagenic effect of motor oils has generally been assayed on Salmonella typhimurium. The results are very consistent. Used motor oil and its aromatic extracts have been found to be highly mutagenic to bacteria. Conversely, new motor oil has not shown any mutagenic effect [29,78–80, 84–86]. In a recent work it has been found that the dimethylsulphoxide (DMSO) extract from petrol engines and diesel engines has the same mutagenicity, and that the unused oil extract can be mutagenic to bacteria [87]. Nevertheless, it appears that used motor oils are more mutagenic than new lubricating oils. This effect can be explained a priori by the fact that during engine operation the oil is contaminated with metals and combustion dust, and principally by an increase in its PAH content. Specifically, the amount of benzo[a]pyrene in the oil increases strongly during motor operation [88].

For petroleum and its products it is generally accepted that the compounds which have a greater carcinogenic effect are the PAH with 4, 5 or 6 aromatic rings and molecular weights between 230 and 300. The various proposed theories are based on certain electronic characteristics of molecular structure [89,90]. The carcinogenic PAH have high electronic density zones, called Kzones, which are easily epoxidized under the action of tissue-associated oxidases and, specifically, under the action of arylhydrocarbon hydroxylase. These studies have shown that PAH are pre-carcinogenic agents and inoffensives in hydrocarbon form. The PAH are epoxidized in organisms by the action of oxidase and hydratase-forming biological reactive intermediates, which are the final carcinogenic compounds [91]. The epoxidation, in certain cases, is not realized in K-zones, such as for benzo-3,4[*a*]-pyrene in which the carcinogenic derivative is epoxy-9,10-dihydroxy-7,8-benzopyrene [92–94]. But, in all cases, the epoxidized derivates of PAH are carcinogenic compounds. The concentration of arylhydrocarbon hydroxylase in the tissues varies strongly according to age, sex, species, and strain of animal, as well as with environmental conditions [95]. External agents, such as PAH, can activate this enzyme [96] and it appears that its activity depends also on genetic factors [97,98].

Some aliphatic hydrocarbons and alicyclic and alkyl-aromatics, all volatile and with long chains of 10-20 carbons (*n*-dodecane, cyclohexyldecane and dodecylbenzene) can participate as synergistic or co-carcinogenic agents. These compounds *per se* have no carcinogenic effect but it has been shown that they increase the frequency of tumors and diminish their induction period. In this way, the effects of benzo[a] pyrene and benzo[a] anthracene in low concentration were increased 1000 times when these compounds were diluted in dodecene [99–101]. These results appear to be due partly to the wetting action of the solvent. Another possible explanation may be the stimulation of microsomal oxidase P-450 and, similarly, arylhydrocarbon monooxygenase. These compounds are not present in the base lubricating oil, because they have different boiling points, but used motor oil can contain this compound type due to fuel (petrol or diesel) contamination. On the other hand, the carcinogenic effect of PAH can also be increased by additives, such as benzyl disulphide, ditert-thiobutyl polysulphide, ditert-thiooctyl polysulphide and some phenols. These additives did not show any carcinogenic effect when they were applied without other compounds [100,102–104].

Topical application of used motor oil from petrol-driven automobiles onto the skin of mice induced local tumours. The incidence of tumours was dosedependent. The used motor oil was applied (dissolved three times in acetone or cyclohexane) twice weekly for 104 weeks while the controls with the solvents induced only 1.5% of mice to produce tumours, the application of 0.625, 1.875 and 5.625 mg of used oil induced 4.6 and 26.6 and 69.4% of mice, respecitively to produce local tumours. The incidences of carcinomas and papillomas were: 100% papillomas with 0.625 mg of oil, 53% carcinomas with 1.875 mg of oil and, finally, 67% cancerous tumours with the application of 5.625 mg of used motor oil [30]. The fraction of PAH containing more than three rings accounts for ~70% of the total carcinogenicity in the case of crankcase oil. This fraction constitutes only up to 1.14% by weight of the total oil sample. The content of benzo[a]pyrene (0.02%) accounts for 18% of the total carcinogenicity of used motor oil [28]. The application of new motor oil to mouse skin did not induced skin tumours [105]. However, an oil additive used in the production of engine lubricating oil (additive containing lead naphthenate) induced tumours in 68% of 35 surviving animals (40 animals originally), of which 75% were carcinomas [106]. Subsequent studies have suggested that the carcinogenic activity of the additive is dependent principally, if not entirely, on the base oil components. The lead naphthenate component was not an important carcinogenic compound [107]. The carcinogenic activity of a base lubricating oil is directly correlated with its PAH content [108].

The effects of inhalation of diesel lubricating oil at a concentration of $63 \,\mathrm{mg}\,\mathrm{m}^{-3}$ or of automobile motor oil at a concentration of $132 \,\mathrm{mg}\,\mathrm{m}^{-3}$ were determined on mice during 11 months. The reported incidence of lung tumours did not appear to be significantly different in treated and unexposed control mice. After exposure to diesel lubricating oil, oil was found in the alveolar macrophages, in the mediastinal lymph nodes and in the lymphatic channels of the lung and pleura of mice, rats and rabbits. Exposure of six monkeys to the motor oil from a petrol engine for 100 days caused the death of two animals, while a similar exposure of seven monkeys to diesel motor oil caused death in six animals. All the monkeys that died had possible infectious pneumonitis, evidence of pulmonary lipophages and exhibited severe hyperplastic gastritis, probably due to swallowing the inhaled oil [109]. No alteration in respiratory function was observed in guinea-pigs exposed to light lubricating oil or multigrade motor oil at concentrations of 10 or 40 mg m⁻³ for 1 h. At 200 mg m⁻³, the light lubricating oil reduced significantly the lung compliance, which persisted for 1 h after cessation of exposure [110]. The aspiration of 0.2 ml of two multigrade motor oils by rats caused, in one case, no mortality after 24 h; however, the second motor oil caused mortality in one of five animals [111]. A group of albino mice exposed to an aerosol of motor oil at a concentration of $4330 \,\mathrm{mg}\,\mathrm{m}^{-3}$ for 92 h showed a deathrate of 14.3%. Oil was found evenly dispersed throughout the lung after 96 h and produced localized foreign-body reactions of moderate severity in the lung, as well as infrequently occurring patches of lipid pneumonia [112].

The embryotoxic and biochemical effects of used motor oil were tested on bird eggs by external application. At 48h of development, duck eggs were exposed externally to 2, 5 or 15 μ l of used motor oil, or 15 μ l of new motor oil. Similarly, quail eggs received proportional doses of 0.5, 1 or 3 μ l of used motor oil, or 3 μ l of new motor oil. The used crankcase oil was highly embryotoxic to both species compared with the new oil and resulted in dose-depdendent mortality, reduced growth and abnormal survivors. Application of 15 μ l of used oil resulted in 84% mortality in ducks, and 3 μ l of used oil resulted in 88% mortality in quail. Abnormal survivors included embryos with subcutaneous edema, incomplete ossification, and eye and brain defects. Red blood cell and liver δ -aminolevulinic acid dehydratase activities and haemoglobin concentration were significantly lower after treatment with used motor oil in embryos and hatchlings of both species. Plasma uric acid, plasma alanine aminotransferase and plasma aspartate aminotransferase were significantly elevated in duck eggs treated with used motor oil before hatching [26]. Reviews on the toxic effects on humans of mineral oils, including a few lubricating oils, are available [4,83,113]. The major human sites affected by the toxicity of lubricating oils are the lungs and the skin. Inhalation, aspiration or ingestion of these materials produces lipid pneumonia and lipid granuloma of the lung. The effects generally observed on the skin are eczematous dermatitis, contact dermatitis, folliculitis, oil acne, lipid granuloma and melanosis. A number of case reports and case series of cancer in association with occupational exposure to mineral oils has been published from different countries [83]. These studies reported squamous-cell cancers of the skin, scrotal cancer, bladder cancer and lung cancer, principally. The International Agency for Research on Cancer [83] was conclusive: There is sufficient evidence for the carcinogenicity of used petrol-engine oils.

MOTOR OIL BIODEGRADATION

In spite of the large number of works on petroleum, petroleum derivatives and hydrocarbon biodegradation, little information is available on motor oil biodegradation. Of the studies performed, all except one were carried out with mixed communities of microorganisms from either marine or freshwater environments or from the soil.

Ludzack and Kinkead [114] studied the degradation of new motor oil by a mixed culture of microorganisms. The mixed culture for inoculation was collected from several sources, including unpolluted rivers, oil-polluted or refinery soils, refinery effluent, and sewage. The microorganisms from sewage were the most active for hydrocarbon biodegradation. The first observation was, after culture, a change in the distribution of the microbial population. The culture was analysed weekly and the motor oil concentration was adjusted to its initial value. The CO_2 production reached its maximal value at the second week and decreased progressively down to very small values after 4 weeks. The oil losses were 64% during the first week and 81% during the second week. The losses were very small during the fifth week. The re-inoculation of culture after 4 weeks enhanced the reactivation to a value of 50%. For cultures inoculated with sewage, with and without motor oil, it has been shown that the oil inhibits the autodepuration process of wastewater. After 4 weeks the CO₂ production of the control, without oil, was more than the cultures with motor oil. These results were obtained from culture seeded daily with 1% by volume of settled sewage. The air recirculation stimulated CO_2 production and also oil biodegradation. The culture temperature was the most important parameter in the biodegradation of lubricating motor oil. At 25°C, 50–80% of the initial oil was biodegraded, whereas at 4°C no degradation was detected.

Walker and Colwell [15] studied motor oil biodegradation in batch cultures prepared with mineral medium containing 2% new motor oil. Mixed microorganisms for inoculation were collected from polluted marine sediment. The authors analysed the oil residue after degradation and determined the fate of the different hydrocarbons: 87% of the aliphatic fraction and 92% of the aromatic fraction had been degraded. The residual oil, after biodegradation, was composed mainly of cyclic alkanes of 1–6 rings. The cyclic alkanes were degraded but at a slower rate than the other constituents of lubricating motor oil.

The same team in a later work [16] compared the biodegradation of new motor oil by microorganisms from marine sediments and seawater. The samples of microorganisms were collected from polluted and seemingly unpolluted points. Two culture types were made up for each microbial population: one with Bay water and the other with salt solution. Microbial growth was, in all cases, greater in the cultures from polluted locations (sediments and water) than in those from unpolluted locations. Also, microbial growth was greater in the cultures from seawater than in those from sediments. Microbial growth was strongly stimulated by the presence of mineral salts. Motor oil biodegradation was higher, obviously, in the cultures with microorganisms from polluted points and also when mineral salts were added. In contrast to microbial growth, biodegradation was greater for the sediment microorganisms than the water microorganisms. This showed that the sediment microorganisms, although producing less biomass, had a greater biodegrading capacity than those of seawater. Analysis of fractions before and after degradation showed that the *n*-alkanes are degraded more readily than the cyclic alkanes. In the culture where the degradation was greatest (sediment from polluted location with mineral salts added), total oil biodegradation was 78%: 82% of the alphatics, 78% of the aromatics and 40% of the resins were degraded.

The biodegradation and effects of used motor oil upon the soil have been studied by the application of used motor oils on the soil surface [22]. The study was carried out with used crankcase oil from petrol engines and diesel engines. The results showed that, after 1 year, 55–82% of automobile oil and 24–53% of truck oil were degraded. Biodegradation during the winter months was very poor and the fertilization effect was more important after 8 months. Fractionation of oil after degradation showed that the soil composition remained virtually the same. With these experiments, no movement of oil added to the soil was observed and most of the degradative activity was carried out in the first 10 cm of soil. However, the products of degradation, such as fatty acids, aldehydes, alcohols, etc., were carried by the runoff water and leachate. The authors also studied the fate of lead contained in used motor oil, and their effects, and motor oil effects in general, on the soil microbial community and plant growth.

Outboard-motor oil is one of the most important sources of hydrocarbon pollution in freshwater environments. The biodegradation of two oil types, one a mineral oil and the other a synthetic oil (polyester based), *in situ* in a lake was much less during the winter season (the water temperature between 4 and 15° C). After 100 days ~ 80% of lubricating mineral oil and 60% of synthetic oil remained in the lake. The degradation rates observed were less than those of petroleum product degradation in the sea. The presence of lubricating additives in the synthetic oil did not affect its degradation, while in the case of mineral oil the absence of additives doubled the biodegradation rate [52]. In a recent work [19], the fate of heavy metals contained in used motor oil was studied during bacterial biodegradation. A large fraction of metals was recovered in the aqueous phase and a smaller portion was immobilized by precipitation, adsorption and bacterial assimilation. Transfer into the aqueous phase can be the consequence of metabolization of hydrocarbons, liberating the metals previously bound or complexed. A proportion of heavy metals found in the aqueous phase was immobilized during bacterial growth. The observed solubilization of metals was dependent on the balance between bacterial growth and hydrocarbon metabolization. This is of importance in relation to the environment, because the transfer involves an increase in heavy metal mobility and, in consequence, their toxicity.

CONCLUSIONS

Most of the 25–28 million tonnes of used motor oil produced yearly is spilled into the environment. Moreover, between 12 and 15 million tonnes of motor oil are dispersed in the environment during motor operation. Only a very small amount of used motor oil is re-refined and the rest is, in one way or another, disposed of into the environment.

Used motor oil is a very dangerous polluting product due to the high content of heavy metals, such as Pb, Zn, Cu, Cd, Cr, Ni, etc. In the environment these metals can be mobilized rapidly by bacterial action. Moreover, used motor oil contains high concentrations of PAH, such as benzo[a]pyrene, which are carcinogenic compounds. The PAH accumulate in the motor oil during engine operation. In this way, the PAH content of used motor oil can be 670 times greater than that of new motor oil. The lubrication additives present in the oils are, in some cases, pollutants.

Spillage of used motor oil onto soil can induce a drastic change in the microbial communities. These changes can affect the biological cycles in the soil. The presence of used motor oil in the soil inhibits plant development and the metal content of surviving plants is increased. In aquatic environments, used motor oil provokes a change in the microbial communities and decreases the primary production of phytoplankton. Heavy metals from used crankcase oil can be transferred to the aqueous phase by bacterial activity. The transfer involves an increase in heavy metal mobility and, in consequence, their toxicity. Used motor oil in aquatic environments can badly damage shell fish and this oil type is one of the primary mutagenic agents in aquatic environments. Most of the used motor oil is burned in inadequate installations. This operation produces large quantities of heavy metal emissions. The emission particles and residue products are ranked to be among the most toxic in comparison with other environmental particles.

Used motor oil is highly mutagenic to bacteria; in contrast, new motor oil has not shown any mutagenic effect. This can be explained by the fact that, during engine operation, oil is contaminated with metals and combustion dust; principally, it is a consequence of an increase in its PAH content. Specifically, the amount of benzo[a]pyrene in the oil increases significantly during motor operation. Used motor oil and its PAH fraction are able to induce carcinomas. These compounds are also embryotoxic to bird eggs by external application. By means of inhalation, aspiration, ingestion or skin contact, used motor oil can induce lipid pneumonia, lipid granuloma in the lung, eczematous dermatitis, contact dermatitis, folliculitis, oil acne, lipid granuloma and melanosis in humans. Finally, used motor oil can induce cancer, principally as squamouscell cancer of the skin, scrotal cancer, bladder cancer and lung cancer.

The environmental biodegradation of used motor oil is only 24-82% in soils after 1 year of application, or 20% in lakes 100 days after spillage. All the preceding considerations support the importance and danger of the pollution due to used motor oil.

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