A COMPARISON OF THE EFFECT OF CLEAN AND WASTE MINERAL OILS ON PERMEABLE PAVEMENTS

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SUMMARY

**During early research on the environmental benefits of permeable paving, clean unused mineral oil was chosen as the standardised contaminant for laboratory tests.
However, as this contaminant did not adequately reflect the kinds of hydrocarbons that would be released in a field situation, it was decided to run a comparative test of the environmental fate of clean and waste oils in permeable pavement models.**

It was discovered that waste oils were significantly enriched with metals such as copper, chromium, zinc and lead when compared with clean oils. However, when using either oil type, the release of oil into effluent was less than 50 mg/l. In addition, the metals in the oil types were not released at high concentrations, being typically much less than 200 μg/l.

**The microbiological communities produced by the two oil types were not significantly different after analysis of the types and number of eukaryotic indicator organisms found both in the effluent from permeable pavement models and upon sampling of the model interior.
This work demonstrates that initial assumptions based on clean oil are readily transferable to a field situation where waste oil forms the bulk of the contaminating material.**

1. INTRODUCTION

Pervious paving systems (PPS) (meant to mean permeable pavements within this context and used interchangeably) are now a tried and tested technology for use within urban water sustainable drainage solutions. Over the last 10 years, research at Coventry University has explored in detail the quality of water discharged from PPS and the underlying mechanisms of water purification and pollution attenuation (e.g. Newman *et al*, 2005).

Pervious pavements have extensively tested at Coventry University and have been shown to retain 98.7 % of a total addition of 1250 g of motor oil added over a four year period (Bond, 1999; Coupe 2004). Extensive biodegradation of this accumulated oil has been proven by the analysis of microbial respiration (Pratt *et al*, 1999). A mixed microbial community, derived from building materials (bacteria, fungi, protozoa and metazoa) contribute either directly or indirectly, to the oil biodegradation process (Coupe *et al*, 2003). This is thought to be via the recycling of nutrients and the maintenance of an actively growing biofilm.

Historically, research into the attenuation of mineral oils within PPS has been achieved using clean unused lubricating mineral oil as the standard contaminant of choice. There were several reasons for using this contaminant. Firstly, even when using a particular type of oil, after time within two different vehicle engines there are likely to be large differences in the composition of the remaining waste oil. Secondly because of point one, the exact used oil composition demands extensive investigation before the oil may be added in a PPS experiment, in order to add a known mixture that can be analysed analytically. This is time consuming, expensive and can require specialised chemical analysis. Finally, it is difficult to determine whether oil is clean or used. Other than the length of time spent within the engine, during which there will still have been wide variations in the distance driven depending on the vehicle, there is no reliable way of definitively stating whether oil is used or clean.

The choice of clean mineral oil of a certain brand and grade has been a mainstay of the PPS research group's strategy and the contaminant of choice throughout the history of oil retention and bioremediation studies.

Despite the successes reported in oil attenuation by PPS (Bond, 1999; Coupe, 2004), it became clear that there were potential problems associated with using a single contaminating substance and not exploring the consequences of employing a more heterogeneous mixture.

These were:

- The presence of toxic metals in used oils at much higher concentrations than clean oils. This brings with it the potential for these compounds to be discharged in correspondingly high concentrations in effluent run-off than observed when using clean oils.
- The presence of increased concentrations of highly toxic organic contaminants such as PAH, monoaromatics such as benzene and toluene in used oils when compared to clean oils (Irwin *et al*, 1997).
- The potential recalcitrance of used oils due to the above factors and a lower degradation rate by the PPS microbes. As the retention and storage function of PPS on the geotextile is essential for pollution prevention, any build-up of free product used oil may over time allow a breakthrough of stored undegraded material reducing the effectiveness of the PPS in the long term.

These concerns led to a research programme that would determine the retention and biodegradation of used and clean oils in a controlled experiment. The effects of the oil type on the microbial community were also assessed, in order to obtain data on the levels of turnover expected depending upon the oil type to be analysed. Analysis of dissolved toxic metals discharged at the base of PPS coming from oil was performed, to determine whether any differences in input concentrations were detectable at the outflow.

2. METHODOLOGY

The first objective was to analyse the composition of the two oil types to determine the levels of metals found within them. It was decided to focus on metals in preference to organics such as PAH, due to in-house analytical capabilities and the fact that many previous experiments had shown at least 98 % retention of added oil masses which would include monoaromatics and PAH. Metals in comparison had received relatively little previous attention from the Coventry PPS research group. The analysis was performed on a Perkin-Elmer ICP (inductively coupled plasma) on the two oil types following extraction into solution with nitric acid and calibration against known standards. The analysis method was performed in the same was as above on aqueous samples taken from the base of PPS laboratory models.

Table 1. Concentrations of some environmentally important metals in clean and used oil (Coupe *et al*, 2005).

Element	New oil mean concentration (PPM) (n=3)	Used oil mean concentration (PPM) (n=3)
Pb	<1	2
Zn	950	1300
Cr	<1	2
Cu	<1	34
Al	1	15
Mo	16	160
Mg	13	490
P	870	1000
Ca	2300	2600

2.1 Simulation of PPS systems

A mainstay of previous PPS work has been the use of miniaturised PPS models referred to as 'rigs' in this paper (see Figure 1). These structures allow a relatively close approximation of a field based PPS to be constructed in the laboratory with the possibility of achieving reasonable levels of replication. These structures also receive artificial rainfall (in the form of distilled water) and nutrient addition in the form of nitrogen, phosphorus and potassium to kick-start oil bioremediation. Rig dimensions, oil application rates, nutrient and artificial rainfall are as shown in table 1. The sub-base arrangement consists of a 300 mm depth of open graded crushed aggregate measuring between 63-10 mm.

Two rigs were used for each oil type giving a total of 4 experimental rigs. Clean mineral oil (Castrol protection plus) and used mineral oil (taken from a Land Rover Freelander after 3 months within the vehicle) was added to the rig surfaces using a purpose-built dripper in order to simulate a leaking engine.

2.2 Analysis of oil in effluent.

Analysis of the concentrations of oil discharged at the base of the PPS was done using a Horiba OCMA oil in water analyser. This apparatus uses S-316 (Trifluorochloroethylene) solvent to extract the oil from water. The instrument gives a digital display reading for oil in effluent concentrations between 1 and 200 mg/l.

Figure 1. Experimental PPS rigs.

Table 2. Dimensions of and additions to PPS rig simulation boxes.

Rig surface area (m^2)	Oil added (g/week)	Rainfall added (ml/week)	Nutrients added (g)
0.041	0.085	280	3.27

2.3 Microbiological analysis.

The analysis of higher eukaryotic organisms, protozoa and metazoa within PPS has long been known to give a good indication of the microbiological health of the system and the levels of biodegradation. Put simply, the more of these organisms there are and the more different types of these organisms there are, the more developed the microbial biofilm and the more robust and stable are the levels of bioremediation (Coupe *et al*, 2003). The screening of effluent samples from PPS models was undertaken routinely (once a week) to determine the density of protozoa and metazoa and the number of taxa represented in rigs. As qualitative differences were anticipated between rigs with used oil and clean oil, the identification of these organisms to the level of genus or species was performed by consulting identification manuals in order to pinpoint any organisms that may be sensitive to possible indicator organisms. The number of different organisms counted per millilitre of effluent over the duration of the experiment was determined by direct counts with a haemocytometer.

2.4 Parallel studies

Running alongside the experiment described in this paper was another laboratory based study to determine the levels of biodegradation in 250 ml culture vessels with and without added NPK nutrients in the form of Osmocote plus® slow release fertiliser. This was done with both used and clean mineral oil and provides a guide as to the ease of biodegradability of the oil types under highly idealised conditions. The results have been presented elsewhere (Coupe *et al*, 2005) but will be displayed below to provide extra information for the interpretation of results.

3. RESULTS

As shown in table 1, the used oil was enriched relative to the clean oil in all the elements displayed. In some cases, such as copper, chromium, aluminium and lead the difference between used and clean oil was either very pronounced or was undetectable or in trace amounts in clean oil but clearly quantifiable in much higher concentrations in used oil. This demonstrates that used oil does represent a contaminant that is enriched in a very important group of diffuse pollutants, the metals.

3.1 Oil attenuation.

Results showing the concentrations of oil released in PPS effluent over time are displayed in Figure 2. The data demonstrate that there is a short-lived difference between the concentrations from used and clean oil rigs. Used oil rigs did display more oil in effluent but at no time did the concentration exceed 45 mg/l. This is retention of 99 % of the added oil however and is even more impressive when considering that the application rate of 17.8 g/m^2 at the surface is approximately 100 times that thought to be deposited at the average urban pavement (Bond, 1999). The spike of elevated concentrations declines over time and this probably occurs partly due to the colonisation and increasing accumulation of biofilm organisms.

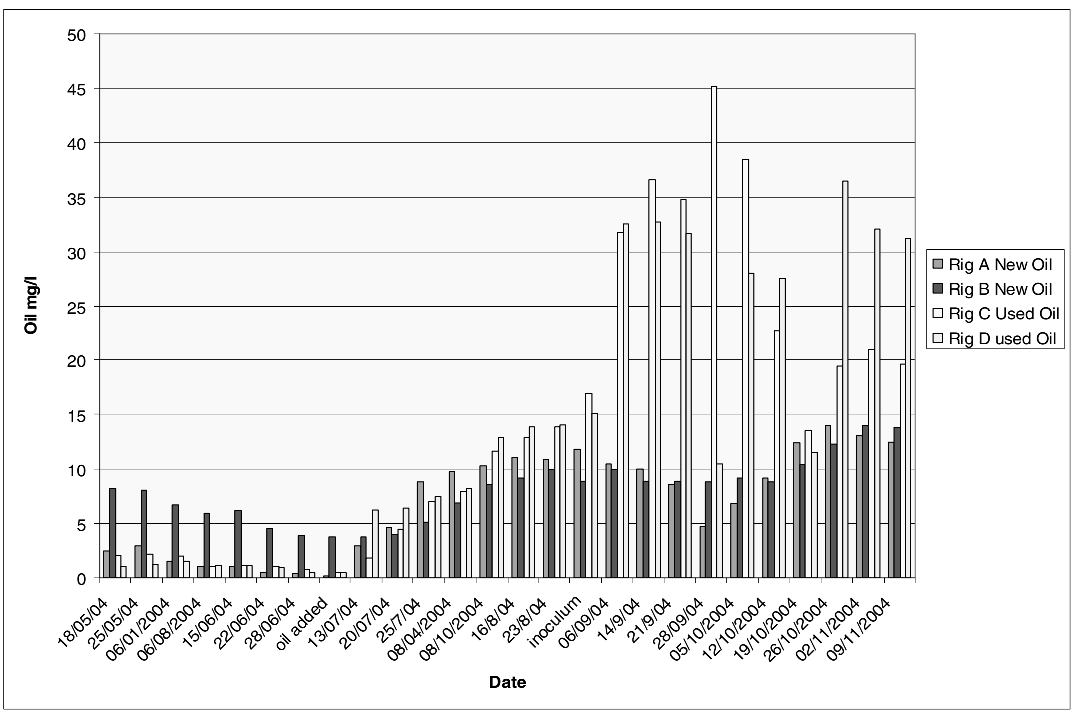

Figure 2. Oil in effluent from used and clean oil PPS rig effluent

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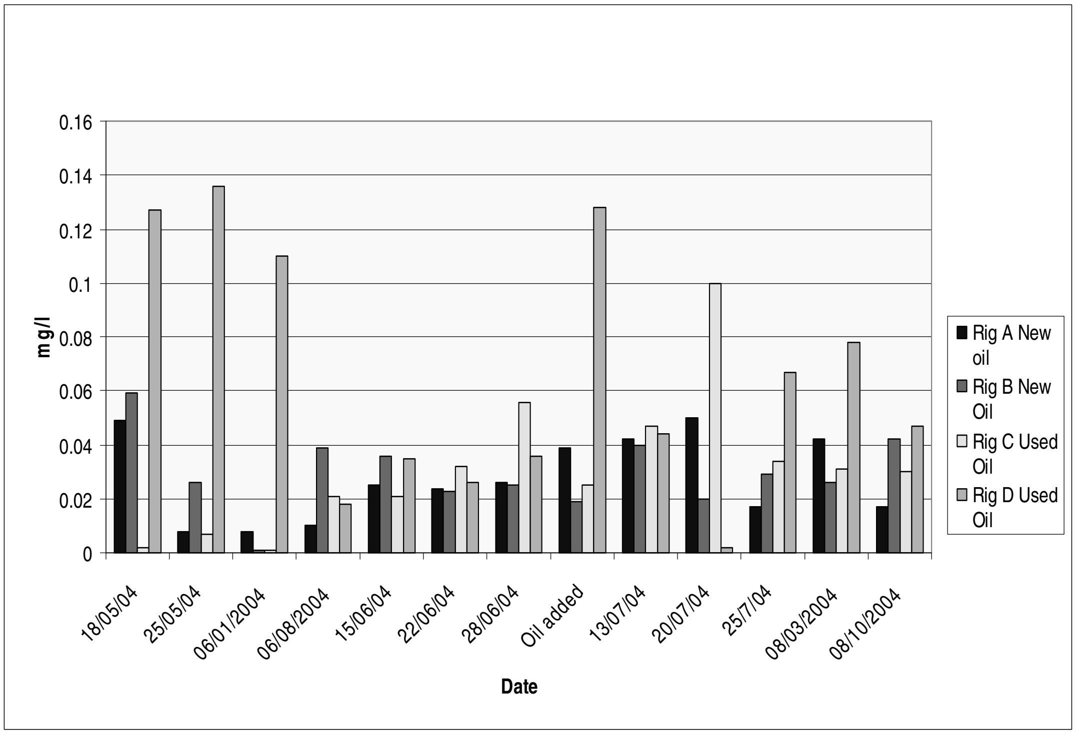

Figure 3. Zinc in effluent from used and clean oil PPS rig effluent.

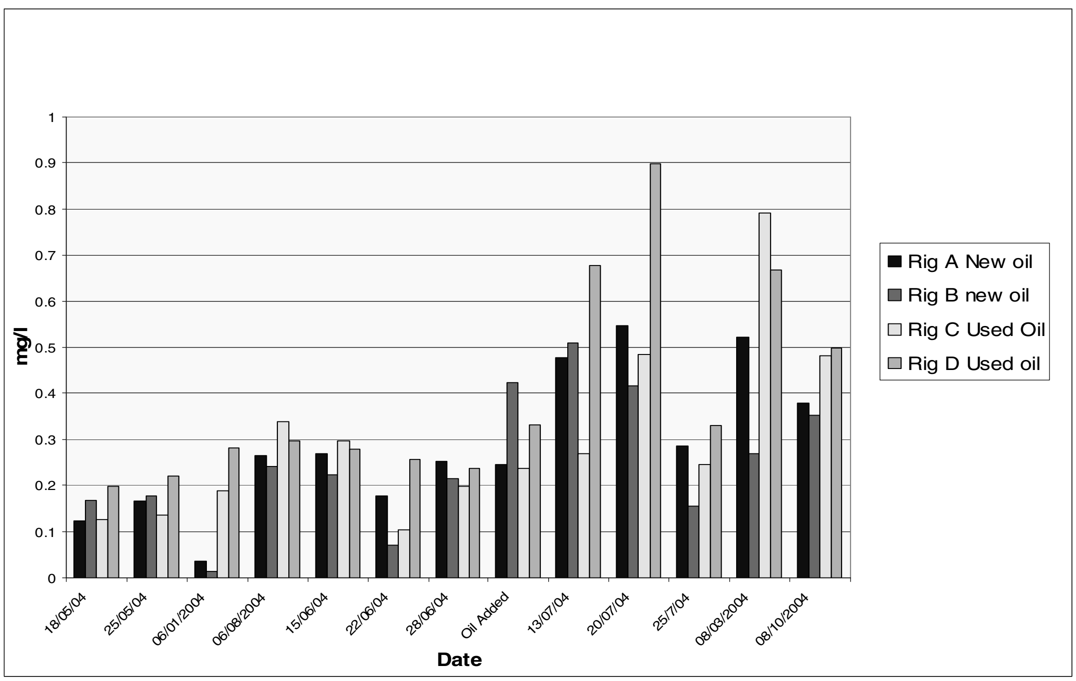

Figure 4. Copper in effluent from used and clean oil PPS rig effluent.

3.2 Metals in effluent

The relatively high concentrations of metals in oil, even zinc in new oil for example, demonstrates that oils act as a considerable source of polluting material both organic and inorganic. Despite the high amounts of metal in the source material, the concentrations in effluent are generally below 1 mg/l despite the 100-fold increase in applied oil compared to the theoretical background levels (Bond, 1999).

There was no clearly identifiable difference in the concentrations released from the rigs despite the differences in metal concentrations in applied oils of both used and clean type. The examples shown below in Figures 3 and 4 display two of the most common and toxic metals in the urban environment. It is worth noting that the differences in concentrations of zinc and copper in used oil before addition to rigs were around two orders of magnitude (zinc 1300 ppm, copper 34 ppm) but the effluent concentrations were no more than one order of magnitude with typically 0.14 mg/l zinc and 0.90 mg/l copper.

Increases in effluent metal concentrations over the 14 weeks of the experiment were minor or non-existent. This indicates that metals will be retained in PPS even where used oils bring greater quantities than clean oils.

3.3 Microbiological results

As shown in Figure 5, the number of eukaryotic taxa identified from the used and clean oil rigs were similar over the first 17 weeks, although increases in taxonomic diversity over the duration of the experiment were slightly slower in the used oil rigs. As can be seen from table 3 however, the final totals of all the taxa recorded from all rigs after six months were remarkably similar to one another and not different qualitatively, particularly as the majority of organisms were common to both rig types.

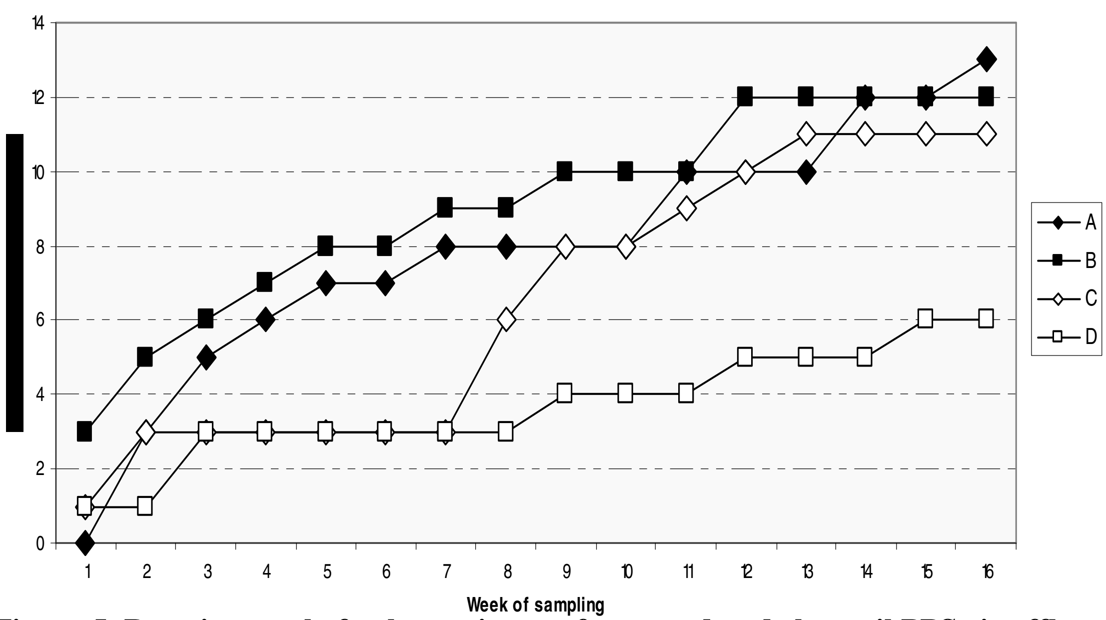

Figure 5. Running total of eukaryotic taxa from used and clean oil PPS rig effluent.

4. DISCUSSION

The attenuation of clean oils was slightly more effective than for used oils but retention of both oil types was very high at more than 99 % for the entire experimental period. The pulse of higher oil in effluent concentrations after 20 weeks may have been due to increased solubilisation due to a bloom of biofilm growth, rapidly attacking the stored product. Even at the highest used oil concentration of 45 mg/l however, this was still well within UK water quality limits for discharge even with 100 times the expected urban loading.

Table 3. Full list of recorded eukaryotic taxa from used and clean oil PPS rig effluent.

Used oil		Clean oil	
Acanthamoeba sp.	Fungi	_Acanthamoeba_ sp.	_Leptopharynx_ sp.
Actinophrys sp.	_Heteromita globosa_	_Actinophrys_ sp.	_*Litonotus_ sp.
Arcella arenaria	_Holophyra_ sp.	_Arcella arenaria_	_Mayorella_ spp.
*Aspidisca sp.	_*Holostichia_ sp.	_Boda caudatus_	Nematodes
*Assulina muscorum	_*Homolazoon_ sp.	_Bodo edax_	*Neuroptera
*Assulina seminulum	_Leptopharynx_ sp.	_Bodo saltans_	_Oxytricha sp._
Bodo caudatus	_Mayorella_ spp.	_Centropyxis aerophila_	_Petalomonas_ sp.
*Bodo celer	_*Monosiga ovata_	_Ceratiomyxa_ sp.	_Pseudoglaucoma_ sp.
Bodo edax	Nematodes	_Cercomonas_ sp.	Rotifers
Bodo saltans	_Oxytricha_ sp.	_*Ciliophrys_ sp.	_*Spathidium_ sp.
Centropyxis aerophila	_Petalomonas_ sp.	_Colpoda cucullus_	_*Thecamoeba_ spp.
Ceratiomyxa sp.	_*Prorodon_ sp.	_Corythion dubium_	_*Trinema complanatum_
Cercomonas sp.	_Pseudoglaucoma_ sp.	_*Cyclopyxis eurystoma_	_Trinema enchelys_
*Chaetospera sp.	Rotifers	Diatoms	_Trinema lineare_
Colpoda cucullus	_*Spumella elongata_	_*Difflugia_ sp.	_Uronema nigricans_
*Colpoda steinii	_Trinema enchelys_	_Euglypha rotunda_	_*Urostyla_ sp.
Corythion dubium	_Trinema lineare_	_Euglypha strigosa_	_Vahlkampfia_ sp.
*Cryptodifflugia sp.	_Uronema nigricans_	_Euplotes_ sp.	_Vanella_ sp.
Diatoms	_*Urotricha_ sp.	_*Flabellula_ sp.	_Vorticella_ sp.
*Euglypha filifera	_Vahlkampfia_ sp.	Fungi	
Euglypha rotunda	_Vanella_ spp.	_Heteromita globosa_	
Euglypha strigosa	_Vorticella_ sp.	_Holophyra_ sp.	
Euplotes sp		_*Lembadion_ sp.	
Total taxa	45	Total taxa	42
Taxa common to both model types			**31**
Taxa endemic to one model type:			*

It may also be the case that the lower viscosity of used oil played a part. The viscosity was not measured quantitatively but was obvious from visual examination. Despite the much higher concentrations of metals in used oil applied at the surface, the concentrations released at the base of the rig models are more or less identical with both oil types and are many times lower than the applied amounts. The mechanism for this retention is likely to be immobilisation on the geotextile as the metals are still a constituent of the oil mass (where a minimum of 98 % applied oil is known to be trapped in all previous PPS oil retention research), and secondly due to absorption and adsorption onto the biofilm that is known to grow extensively over the geotextile. This secondary biological mediation of oil has not been sufficiently investigated, but it is the opinion of the research group that such extensive and vigorous biological growth may have a 'fine filtering' mechanism, therefore contributing to both retention and biodegradation processes.

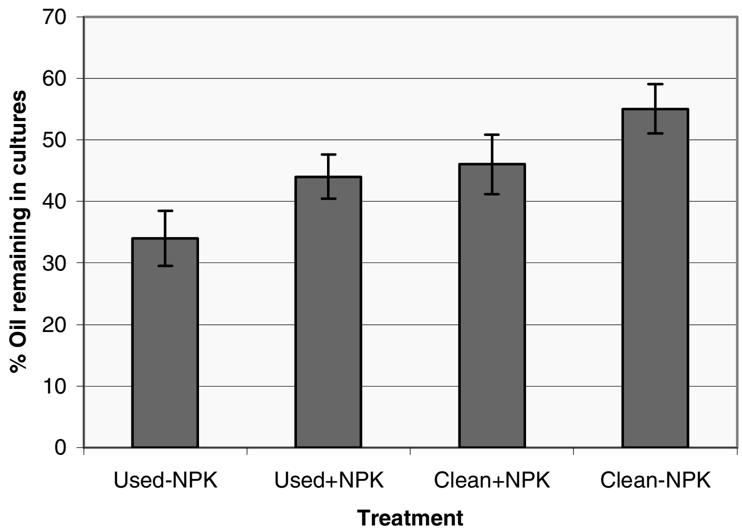

Figure 6. Clean and used oil degraded with and without nutrients in 250 ml culture vessels. Oil addition at the start of the experiment was 2 grams per litre. (Coupe *et al*, 2005)

Analysis of the eukaryotic fraction of the PPS effluent has shown only a slight difference in the number of microbial taxa appearing over time from the two rig types and little or no difference in the communities produced in the longer term. The similarities between the microbial taxa identified in this experiment, shows that the used oil rigs, with much larger metal burdens do not give rise to a pauperised eukaryotic community. As discussed in the introduction, this is an important result as it indicates that rig microbial processes are acting in a similar way, even when organic and inorganic compounds are enriched compared to previous studies. From this is can be assumed that biodegradation is occurring at similar rates to those in clean oil rigs, with around 40 % biodegradation of stored product in 6 months (Bond, 1999).

Further evidence of the rapid breakdown of used oils and the tolerance of microbial communities of high metal and organic concentrations was reported by Coupe *et al*, 2005. In this experiment, running parallel to the results presented in this paper it was shown that even where no nutrients were added to oils in water based laboratory cultures, significant oil degradation may take place (see Figure 6 below). As can be seen if anything, the addition of nutrients hindered the biodegradation of both clean and used oil in this study. The implications of this are two fold. Firstly, as this experiment was conducted under strictly sterile conditions except for the oils themselves, it is clear that oil must contain organisms that can break down the substrate from which they originate A higher loading of dormant or encysted microbial species in used oil when compared to clean oils may partly explain the higher used oil degradation rate. Secondly, if nutrients are not provided it does not necessarily mean that oil biodegradation will not occur. Indeed the higher biodegradation rate reported above without any additional NPK shows that the nutrients within oil must be accessible to the biological components of oil.

The colonisation of used lubricating oils has been reported previously and from drilling fluids used in oil exploration (Nweke and Okpokwasili, 2003) and this result also shows that used oils are susceptible to attack despite their highly toxic components. As the experiment above was carried out under conditions that were highly idealised and non-representative of a PPS environment, applying the results to the PPS are not strictly valid. It is of great importance to observe that the retention of used oil and the metals within it occurs almost as well as with clean oil. PPS microbial aggregates are not affected to any significant degree by used oil and indeed, where used oil is spilled without any added nutrients, it is worth noting that the oil will still be degraded.

5. CONCLUSIONS

The addition of used oils in place of clean oils in PPS retention and biodegradation studies does not lead to a catastrophic failure of the efficiency of the PPS system. A short lived pulse of higher oil-in effluent concentrations was observed but this did not threaten to breach UK surface water discharge limits. Negative biological responses to used oil were not conclusive in the shorter term and not observed at all over the full term of the experiment despite much higher metal concentrations in used oil. Placing these results alongside previous work from the Coventry group supplements the view that oil retention rates have not been overestimated. The need for nutrient application to stimulate biodegradation, although justified no doubt in some cases, may not be necessary if maintenance budgets are not in place to cover these costs.

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