MAINTENANCE OF OIL-DEGRADING PERMEABLE PAVEMENTS: MICROBES, NUTRIENTS AND LONG-TERM WATER QUALITY PROVISION

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SUMMARY

Oil degrading pervious paving systems PPS (meant to mean permeable pavements within this context and used interchangeably) have been demonstrated to require little maintenance, despite functioning as a very effective trap and *in-situ* bioremediation device, for urban-derived pollutants. Our work has shown that providing the micro-organisms with inorganic nutrients through the use of liquid fertilisers is not effective over extended periods. The slow release fertiliser used by our group has been shown to be effective but the need to replenish this and some problems with the release of pulses of nitrogen and phosphorus has indicated that in great care needs to be taken with such nutrient sources. Using large scale outdoor experiments it has been shown that for Nitrogen and Potassium there is an adequate input from the structure itself and from external inputs. Recently it has been discovered that other nutrients such as phosphorus are present within waste oil. These resources have been shown to be available to pavement microbes and this, added to diffuse sources such as leaf litter or those dissolved in rainwater, may be enough to maintain long-term oil degrading activity without additional inputs. There is still, however demonstrable advantages in providing some additional phosphorus. The widespread acceptance of sustainable technology depends on low maintenance costs and a record of reliability. In this paper we also report some of the efforts being made to address the long term phosphorus issue.

1. INTRODUCTION

Hydrocarbons require an appropriate nutrient status to convert the compounds into useful intermediate substances for metabolism and ultimately cellular material. Many types of nutrient are needed for this process. Macronutrients are needed in relatively large quantities and a shortage of nitrogen, phosphorus or potassium will lead to sub-optimal biodegradation rates. Micronutrients including a number of trace elements are needed in much smaller amounts but, as will be shown, they can make a difference to bioremediation in PPS systems. In many biodegradation situations either nitrogen or phosphorus (or both) are the limiting factor in generating the biological population capable of braking down hydrocarbons. An application of 3.2 mg of ammonium nitrogen and 0.6 mg of phosphate degraded Kuwaiti crude oil at a concentration of 70 mg per litre of oil (Atlas, 1981). A carbon to nitrogen ratio of 10:1 and carbon to phosphate at 100:1 has been suggested for stimulation of crude oil biodegradation in seawater (Atlas and Bartha, 1973) and similar ratios are to be expected in freshwater situations. Micronutrients are needed in much smaller doses and, although their absence is less important, their presence in useful quantities has been shown to stimulate higher biodegradation rates in pervious pavement systems (Bond, 1999, Pratt *et al.*, 1999).

The rate of hydrocarbon biodegradation is heavily influenced by the concentration of usable nutrients within the contaminated area. Degradation processes do occur within the natural environment but at a relatively slow rate (Rosenberg *et al.*, 1992, Atlas and Bartha, 1987). Slow release inorganic fertilisers have been used to degrade oil in marine ecosystems: a $MgNH_4PO_4$ mixture added to an oil slick degraded 63% compared to 40% in an untreated control (Olivieri *et al.*, 1976). As reported by Lee and Tremblay (1993), application of soluble inorganic and slow release formulation fertilisers to a low energy shoreline demonstrated that at temperatures above 15°C the coated slow release formula was very effective in boosting biodegradation. Below 15°C, soluble fertilisers used for comparison allowed greater nutrient release. This was proposed as the reason for relatively higher rates of degradation by liquid fertilised systems than those stimulated by slow release fertilisers when operated at lower temperatures.

Within the Permeable Pavement Research Group at Coventry University attempts were made to utilise Urea Formadehyde as a nitrogen source but the method of manufacture caused problems with residual methanol inhibiting microbial growth (Roemer, 2001). Attempts were made to create a methanol free polymer but this work was never taken to conclusion because of more promising leads which will be discussed later. However other workers have had success with this source of nitrogen. For example Rosenberg reported slow self-cleansing rate of a crude oil contaminated beach as compared with the rate when supplemented by a urea formaldehyde polymer containing 18% N and 10% P_2O_5. In the study the biodegradation of 86% of the total oil in treated plots was observed, with a decrease from 5.1 mg of oil per gram of sand to 0.6 mg in 28 days. Seasonal rates of degradation were 0.06 mg per g sand in winter and 0.13 mg per g in summer.

Remediation of crude oil on beaches close to the site of the Exxon Valdez spill in 1989 demonstrated that of the available technologies for clean up, the addition of suitable nitrogen and phosphate proved the most effective and the least likely to result in further ecosystem destruction (Swannell *et al.*, 1996). This was in comparison with warm and cold-water washing, steam cleaning and manual oil recovery. Much of the available evidence highlighted a need for inorganic fertilisers in order to stimulate the process of biodegradation. Although the rate of biodegradation may be generally slow, due to factors such as the relative toxicity or recalcitrance of oil (in conjunction with factors such as temperature and water availability), bioremediation remains an efficient use of resources compared with many of the alternatives discussed by Swannell *et al.*, 1996.

Several studies have found that the addition of N and P to water increases the bacterial decomposition of hydrocarbons. Fertlisation with N and P has been found to be particularly important in situations where the lack of nutrients and high carbon content of the oil limits the rate of biodegradation (Atlas & Bartha, 1972; Venosa, 1996; Swannell, 1996).

From the start of our investigations into oil degradation within pervious pavements studies (Pratt *et al*., 1999) has shown that the availability of inorganic nutrients (particularly nitrogen, potassium and phosphorus) in this system is a limiting factor for the sustained health of the bacteria required for oil biodegradation in laboratory model structures.

Since 1995 several hundred PPS model systems have been established in our laboratory. In every case, where oil and nutrients were added to a PPS model in the laboratory the added oil was shown to be degraded. The organisms making up the PPS system have demonstrated considerable resilience to changes in the environment and have remained in oil degrading operation for over 5 years. The highly optimised conditions in most of our laboratory systems would of course not be found in a field situation. It is more likely that the biodegradation process would be seasonal in nature with summer temperatures increasing the activity of the community. Since in the absence of a major spillage the

expected accumulation of oil is thought to be 100 times less than that routinely applied to our long term model system, the retentive properties of the geotextile would assist the storing of hydrocarbons until the 'growing season' for microbial aggregates the following spring. Since it is very rare for the UK to experience no rainfall for more than a few days, the possibility of the geotextile drying out in a similar seems remote. Indeed, the observed response to dry conditions would appear to make the PPS suitable for areas commonly experiencing a more prolonged drought. The rapid response of microbial communities to hydrocarbon contamination is also encouraging for field based PPS systems. Since drips of hydrocarbon from a parking area would occur in an almost random pattern, it would not be possible for local microbial aggregates to be fully adapted to oil degradation when the spill occurred. However the retention capacity of the geotextile would hold the spill in place until the community was able to degrade it.

2. LONG TERM BIOREMEDIATION EXPERIMENTS

The longest published series of respiration measurements in an oil degrading PPS is the 1200 day plus series which was started by Bond (1999) and completed by Coupe (2001). It was carried out using a 600mmX 600mm full cross section of a 50mm granite sub-base pavement housed in the test rig previously described (Bond, 1999). This test rig was provided with ports for sampling air (for carbon dioxide and oxygen determination) from within the pavement at the level of the bedding layer and the subbase. Throughout the experiment respiration in the bedding layer was higher than in the subbase. Figure 1 shows the data obtained for the bedding layer samples over a period of 1220 days. During the experiment rainfall was applied at a rate equivalent to the average rainfall for London except that there were a number of drought periods. Oil was applied weekly, except for vacation periods corresponding to scheduled oil addition days. Throughout the 1220 days a total of just over 3kg per m2 was added.

The results of the first 1220 days of the experiment are shown in Figure 1. This shows the results of monitoring carbon dioxide and oxygen in the sub base of the structure. From the date when the slow release fertiliser (Osmocote) was added there is an elevated carbon dioxide and reduced oxygen in the structure (this continues to the time of writing without addition of extra fertiliser). The rapid fall after day 755 was due to an artificially
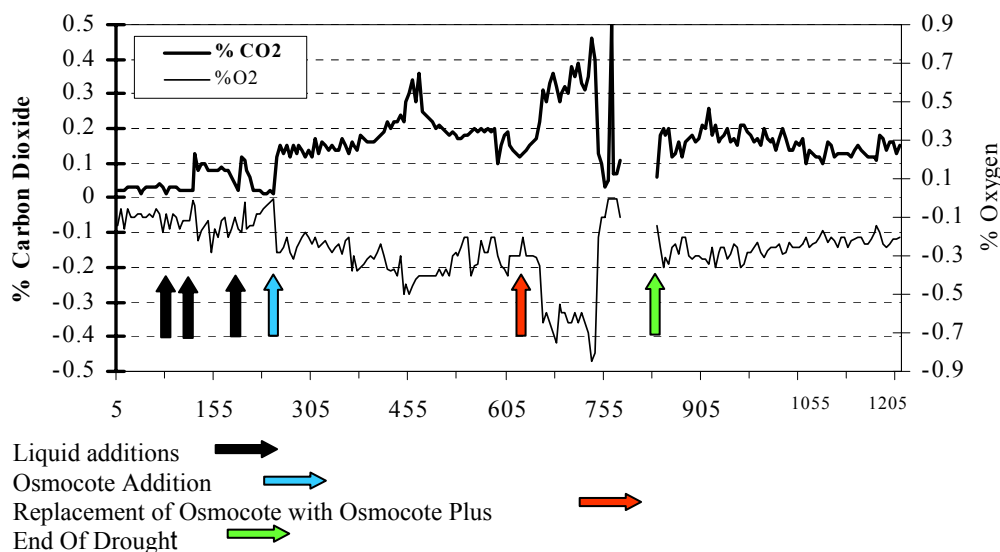

Figure 1. Carbon dioxide and oxygen concentrations in bedding layer.

induced drought in the structure started on day 650 but even after over 150 days of drought the system recovered quickly when rain was again applied. The spike in carbon dioxide (not mirrored by a dip in oxygen), just after the drought, may have been due to an instrument malfunction or possibly due to a release of carbon dioxide from carbonates in the structure as dying micro-organisms released acids when they decayed. There is, unfortunately, a gap in the data which represents data loss from the computer just after the drought period.

It can be seen that the activity reaches a peak about 200 days after slow release fertiliser application but that the fall off is very slow. A further, (higher) peak in activity is reached about 150 days after Osmocote Plus activation. But even after approximately 57 weeks with rain (i.e. ignoring the days of the drought) there was still an activity in the test rig which is as good as any which was achieved with the liquid fertiliser. It is estimated that the activity could be maintained at an acceptable level for at least 1 year for a single fertiliser application.

Partway through the experiment it was decided that the application of inorganic nutrients, albeit in the form of slow release fertiliser, might be causing release of these nitrogen and phosphorus as potential pollutants. Figures 2 and 3 show the results from day 375 to day 740 of the experiment for N and P respectively. These figures show that there was a relatively low level of nitrogen and phosphorus in the effluent but that when the fertiliser pellets were first applied the N and P levels rose to 16 and over 5 mg/l respectively with typical levels outside these first flush events around 1mg/l for both. This issue is addressed below.
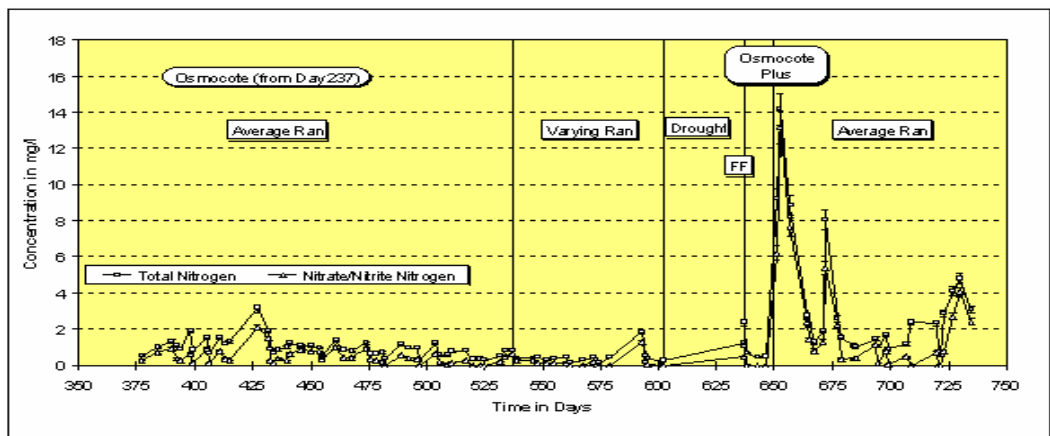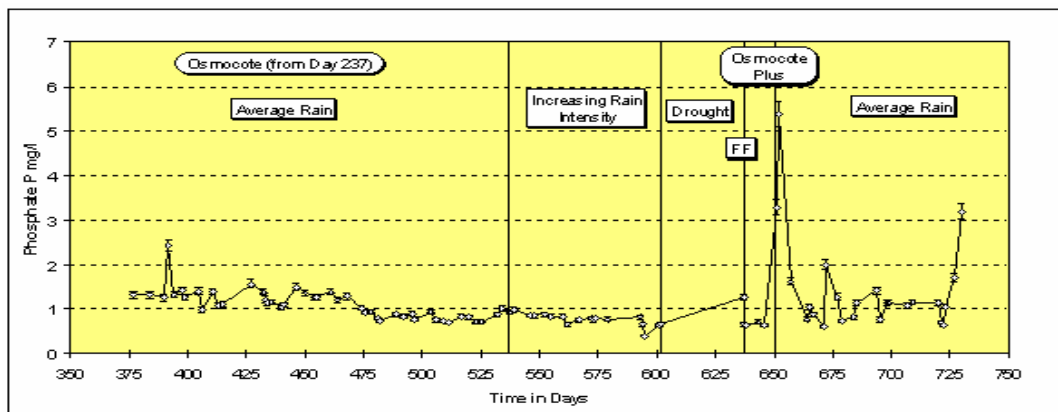

Figure 2. Nitrogen release from fertilized PPS test rig

Figure 3. Phosphorus release from fertilized PPS test rig

3. QUANTITATIVE BIOCHEMICAL STUDIES

When the expertise became available to the group through collaboration with the Rothamstead Experimental Station a further experiment was carried out to try to quantify the effects of inorganic nutrients on oil degrading biofilm formation on the geotextile, the part of the porous pavement which has been shown to be responsible for the detention and biodegradation of oils (Bond, 1999). Biofilm formation was studied on isolated heat bonded polypropylene/polyethylene geotextile samples provided with water and oil (concentration equivalent to solubility of used oil in water and nutrients when appropriate at an application rate of 10 g Osmocote Plus per m^2). The geotextiles were examined after 20 days using electron microscopy and by measuring the amount of ATP per unit area of geotextile (Contin *et al.,* 2001). Figure 4 (a-d) illustrate the difference in biofilm with low magnification and high magnification SEM images (samples mounted on double sided carbon mounting pads and gold coated). Clearly there is a much stronger visible biofilm on the geotextile supplied with inorganic nutrients and the ATP activities were 0.6 and 0.02 nmol ATP /cm^2 for the with added nutrient and without added nutrient respectively a 12 fold difference in activity.
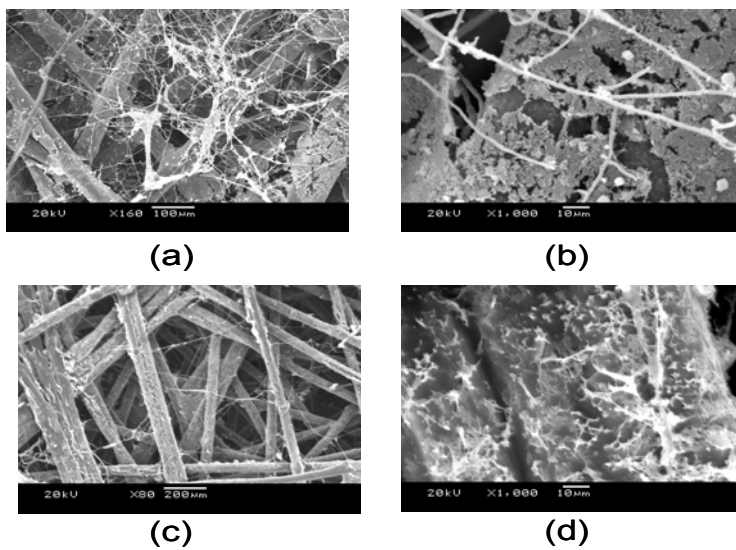
(a)

(b)

(c)

(d)

Figure 4. Electron micrographs showing biofilm density
(a) & (b) with added nutrients (c) & (d) without added nutrients

4. PRACTICAL ISSUES

Clearly there is significant advantage for biodegradation when additional inorganic nutrients are made available. In laboratory model systems however there are less of an external input and the question now asked is whether this advantage is real in practice and whether it applies equally to all the inorganic nutrients. This was studied by Jenkins (2002) on a full size car park model with 6 bays paved with Permavoid Aquaflow blocks. The system was built as tanked installation with the effluent directed to an inspection chamber for collection. The pavement had been in use as a car park at Coventry University for 6 months and the process was carried out during the months of April and May. Before the addition of any fertilizers the NPK concentrations were measured in the effluent when available through natural rainfall. Nitrogen and Potassium were present in relatively high concentrations (2.5 and 25 mg/l respectively. It was postulated that N was coming from windblown

leaves and animal urine and faeces and that K was derived from the minerals used in construction. For Phosphorus however the concentrations were much lower. Originally the method used to detect Phosphorus lacked sensitivity but when a suitable method became available the measured concentrations in the effluent were around 0.05 mg/l. After the addition of Osmocote Plus by brushing fertilizer granules into the infiltration channels of the pavement at a rate of 25g/m^2 there was a pulse of nitrogen through the system giving a concentration of 50mg/l in the effluent. The phosphorus levels were much lower with a peak of 0.17 mg/l but double the level normally required for phosphorus in most storm water discharges. This was much less than was measured by Bond (1999). It was proposed that the pulse was caused by an inability to ensure that all of the fertilizer granules were put out of the reach of traffic tyres and thus some were being crushed, releasing the whole of their fertilizer load instantaneously.

We are therefore faced with a dilemma. If we do not apply fertilizer the biodegradation is probably limited by the phosphorus availability. Even if we could obtain slow release fertiliser granules containing phosphorus only there would be unacceptable pulses of P from time to time as the P was replenished. We proposed that if phosphorus enrichment was to be used we would need either to create a long-life slow release system that released phosphate slowly and ideally at the point of biofilm production (i.e. the geotextile itself) or find a mechanism to remove the phosphate from the effluent after contact with the geotextile but before either infiltration below the structure or out flow from a tanked system. The use of limestone or recycled concrete in the subbase was a possible approach since phosphate should precipitate as apatite under high calcium conditions .This showed initial promise in laboratory trials with oil retention and biodegradation found to be as good as when using a granite substrate. However following experience of the rapid deterioration of a field based recycled concrete system this was discontinued in favour of using zero-valent iron, a technique borrowed from the use of reactive barrier walls used in contaminated land applications. Again this approach was bearing fruit and remains a possibility but the progress made in the direction of a phosphate loaded geotextile was so promising that resources have been directed towards this approach.

5. SELF FERTILISING GEOTEXTILE

This section of the paper presents research into the development of a self-fertilising multi-component geotextile mat for use in PPS. It is intended that this geotextile will provide the slow release of required inorganic nutrients over an extended time period (ideally 20 years). Included here are some of the initial results on the testing of a novel slow release fertilizer framework to be incorporated within the geotextile, including its ability to sustain an oil-degrading bacterial colony in a laboratory simulated PPS. The details on the manufacture of the beads are available elsewhere (Spicer *et al*., 2005). The nutrients stored and released for these studies were nitrogen and phosphate in the form of ammonium phosphate. The geotextile was spun from polymer fibres (either polypropylene or polyethylene) containing 1% wt nutrient releasing spherical beads (1.3 μm in diameter) nominally called μ-Sq beads. These beads comprise a novel organic polymer that is produced in the form of spheres of uniform diameter, as shown in Figure 5(a). Figure 5 (b) shows an image of the geotextile produced using these beads with the beads protruding from the surface. When soaked in ammonium phosphate / phosphoric acid solution for 30 minutes at 5°C they absorb 7% w/w of phosphate (in the form of ammonium phosphate) and upon contact with water the nutrients are released at concentrations of up to 14mg/l. As can be seen in Figure 6 much more controlled release of phosphate is achieved under simulated rainfall conditions (Spicer *et al.* 2005) when the beads are spun into polymer fibres, reducing the equilibrium concentration of phosphate

(a)   (b)   (c)
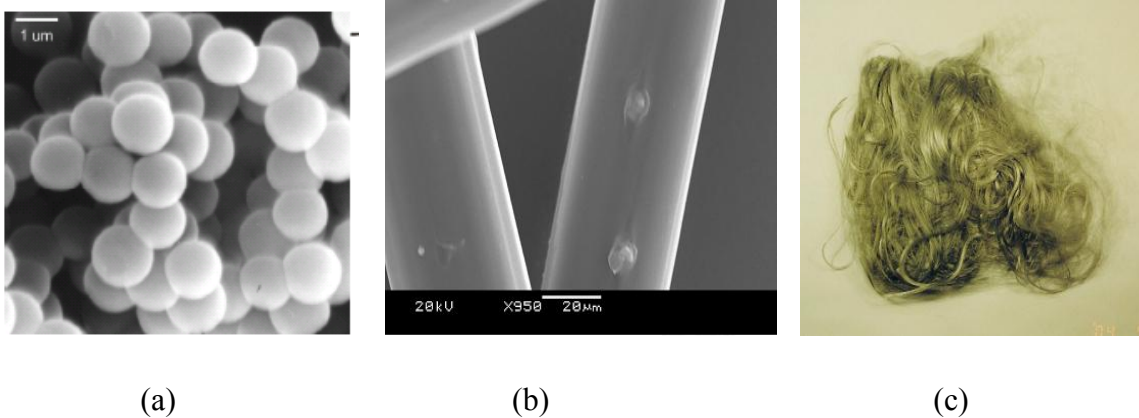
Figure 5. Organic beads utilized as a carrier for inorganic nutrients (a) neat beads (b) beads incorporated into fibres. (c) spun fibres containing fertilizing beads

in water in contact with the fibres to less than 0.05 ppm, a level which would normally not be suitable for sustained bacterial growth but it has been shown that because the nutrients are able to be scavenged from the fibres by the microorganisms the biofilm can be established without the risk of loss of excess nutrients. It has also been established that once the oil degrading bacteria are established a microbial assemblage capable of recycling the available nutrients with the majority of nitrogen and phosphorus tied up as biomass.
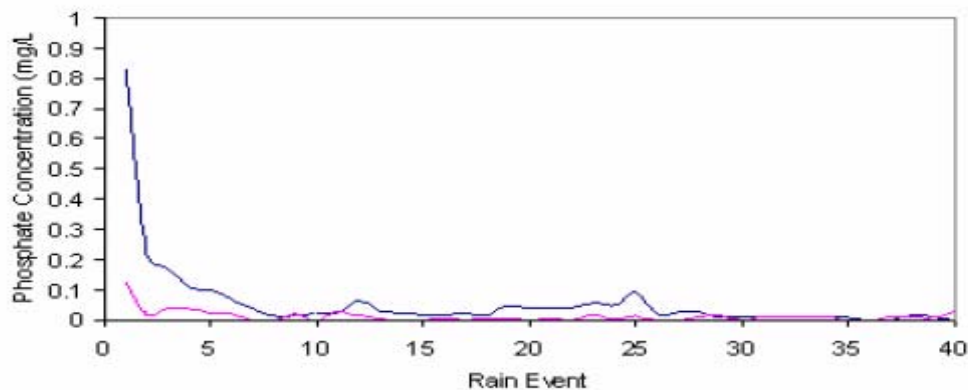

Figure 6. Release of P from polypropylene fibres (blue) and low density polyethylene fibres (red) under simulated rainfall conditions.

Eight PPS models were constructed from acrylic with the dimensions 30 cm x 12 cm x 12 cm. Recycled granite was used for the sub-base layer, then a 2 cm layer of gravel and finally a concrete block paving brick on top which had been cut in half, and a 1 cm hole drilled through the centre to allow for oil and water additions to the centre of the models. A layer of geotextile was placed beneath the subbase and another on top of the sub-base below the gravel. The top geotextile layer held 10 g of either phosphated polypropylene fibres (1% phosphated μ-Sq beads - 4 models) or blank polypropylene fibres (4 models) spread evenly across the geotextile. The models were completely sealed at the start of the experiment, and water and oil added via a wide bore needle through a suba-seal in the acrylic lid of the models, delivering these directly into the central hole drilled into the block and onto the geotextile fibres.

0.84 g of clean motor oil was added each week prior to the rain which was 102 mL of distilled water, corresponding to an annual rainfall of 594 mm, the average amount quoted for London (in Bond, 1999). Both the oil and rain amounts are in accordance with those previously used for PPS experiments (Pratt *et al*., 1999; Coupe *et al*., 2003). Phosphate levels in the effluent were analysed using the molybdenum blue method with ascorbic acid. The levels determined ranged between 0.25-0.45 mg/L, averaging 0.28 mg/L. Hydrocarbon levels using a Horiba analyser were used for the oil analysis. This has shown that all the PPS models are retaining over 99.97 % of the oil introduced. Microbial activity was measured using fluorescein diacetate (FDA) hydrolysis using the method Spicer *et al.* (2005) was modified by Coupe (1995) from a method reported by Schnurer and Rosswall (1982.). Figure 7 shows the difference in microbial activity in the effluent samples for phosphated and non-phosphated geotextiles respectively with the phosphated fibres showing double the activity within 9 weeks,
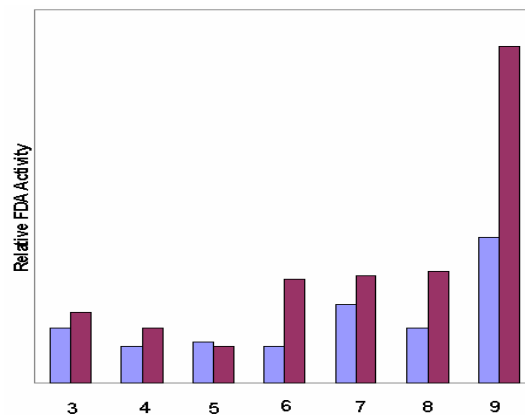

Figure 7. Relative FDA activity for rain events 3-9 for phosphated (red) and non-phosphated (blue) fibres

Carbon dioxide measurements were also made and these indicated a similar level of advantage (Spicer *et al.,* 2005).

6. CONCLUSIONS

The fact that addition of inorganic nutrients is essential for laboratory experiments on oil degrading PPS systems has been demonstrated. The need for the application to long term real systems is less certain but there would be a definite advantage in terms of the rate of biofilm development following initial exposure to oil. A variety of methods are available which might achieve the aim of adding inorganic nutrients without risking them becoming a water pollutant in there own right and there is great potential for a slow release nutrient system being incorporated into geotextiles. At the time of writing the cost of the organic beads would appear to be prohibitive but research is under way to develop cheaper alternatives now that the principle has been established. As long as the added nutrients can be proven to be 'locked up' within the system, regulatory bodies should view these developments in a positive light.

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