Laboratory-based experiments to determine the impact of application of glyphosate-containing herbicides (GCH) on the water quality role of pervious paving systems (PPS)

Etude d’impact de l'utilisation des herbicides contenant du glyphosate (GCH) sur la qualité de l'eau. Examen de la technique des revêtements perméables (PPS)

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RÉSUMÉ

Les expériences en laboratoire testant des revêtements perméables sur des plates-formes (PPS) visaient à déterminer l'effet des herbicides contenant du glyphosate (GCH) sur la capacité de rétention des polluants des PPS. Le polluant utilisé était de l’huile de moteur usagée et les résultats ont révélé que les GCH perturbaient la capacité des PPS à retenir les hydrocarbures (HC), dès l’instant où ils ont été introduits dans des concentrations de plus en plus importantes. Les concentrations de fond étaient indétectables, mais les plates-formes utilisant à la fois du pétrole et du GCH ajouté atteignaient plus de 70 mg l-1 d’hydrocarbure, tandis que celles qui utilisaient seulement le GCH atteignaient 25 mg l-1 d’hydrocarbure. L’opacité observée dans les effluents des plates-formes utilisant le GCH ajouté a été confirmée par des mesures de turbidité, qui indiquaient que plus forte était la concentration de GCH ajouté, plus forte était la turbidité. Des valeurs de pH mesurées ont diminué avec le temps, en particulier dans les plates-formes avec GCH. Il a été estimé que le pH et la turbidité étaient impliqués dans le rejet de métaux lourds, en particulier le plomb et le zinc, ce qui était préoccupant en raison de leur proximité avec les limites fixées en 2011 par l'OMS pour la qualité de l'eau potable. Il a été conclu que l'agent tensio-actif dans la formulation du GCH est probablement à l’origine d’une émulsion du pétrole, présentant des niveaux élevés de métaux, qui s’infiltre ensuite dans le géotextile, là où se produit généralement la biodégradation du pétrole, et se répand à travers la couche de base du PPS. Cette étude a suscité des inquiétudes quant à l'impact que les formulations GCH couramment utilisées pourraient avoir sur la qualité des eaux réceptrices, d’autant plus que la législation récemment adoptée au Royaume-Uni encourage l'utilisation de systèmes de drainage durables et donc des PPS.

ABSTRACT

Laboratory-based experiments using test pervious paving (PPS) rigs were used to determine the effect of glyphosate-containing herbicides (GCH) on the PPS’s pollutant retention performance. The pollutant used was used engine oil and results found that GCH disrupted the ability of the PPS to retain hydrocarbons (HC) since they were released in increasing concentrations over time in the rig effluents. Background concentrations were below the limits of detection, but rigs with both oil and GCH added reached over 70 mg l^{-1} HC whilst those with just GCH applied reached 25 mg l^{-1} HC. Cloudiness observed in the effluents from rigs with GCH added were confirmed by turbidity monitoring whereby the higher the concentration of GCH added, the higher the turbidity. Measurement of pH declined with time, particularly in the GCH rigs. Both pH and turbidity were thought to be involved in the release of heavy metals, particularly Pb and Zn, which were of concern as they were close to WHO 2011 potable water guidelines. It is concluded that the surfactant in the GCH formulation may be forming an emulsion with the oil, which is shown to contain high levels of metals, and this is then pushed through the geotextile, which is where biodegradation of oil usually takes place, and washes out through the PPS base layer. This study has raised concerns regarding the impact commonly used GCH formulations may have on receiving water quality, particularly with the introduction of legislation recently in the UK which encourages the use of sustainable drainage systems and therefore PPS.

KEYWORDS

Geotextile, Glyphosate-containing herbicide, Pervious paving system, Sustainable drainage

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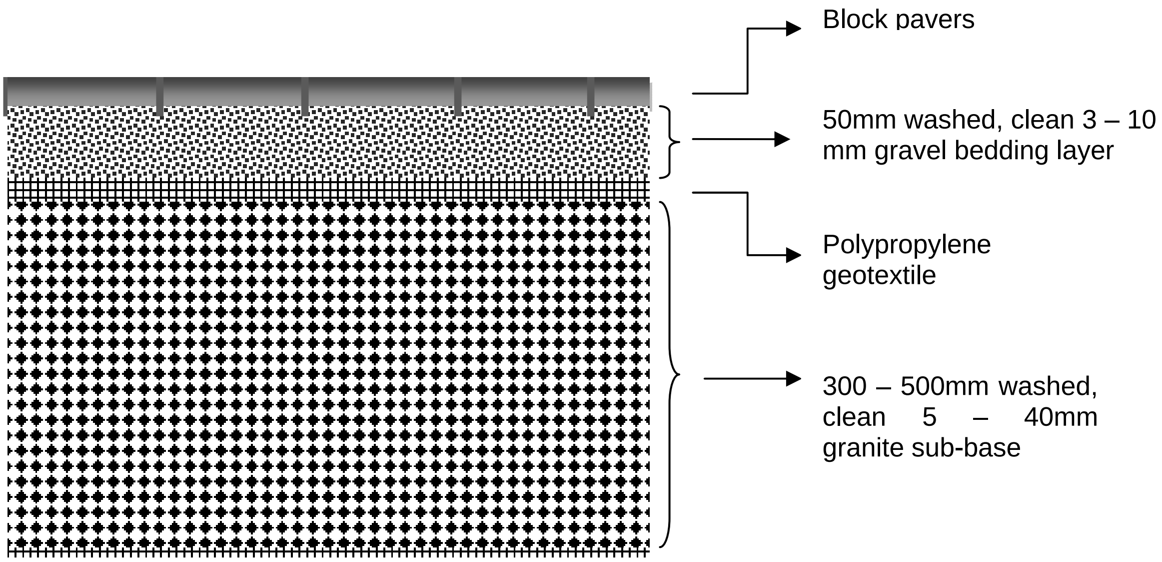
1 INTRODUCTION

Sustainable drainage (SUDS) is a means of attenuating the storm peak by encouraging infiltration, storage and conveyance of excess stormwater, essentially mimicking the natural process of dealing with floodwaters (Charlesworth et al., 2003). This is achieved using SUDS devices individually or designing them into a train. One of the devices used for this purpose is the PPS, essentially hard infrastructure which allows water to infiltrate and then it either passes into groundwater, or the system can be tanked and the infiltrating water stored for another use. Fig 1 shows a generalised cross section of a PPS which utilises block pavers as the surface course and includes a geotextile between the bedding layer and sub base. This has 2 practical functions, firstly it separates different sizes of aggregate to avoid blocking; Fig 1 shows it separating the 3-10 mm gravel bedding layer from the 300-500 aggregate in the sub base. Secondly, it allows a hydraulic head to build up above its surface before the pressure of water is forced through the permeable fabric. Whilst the water is held above the geotextile, particulate associated pollutants (PAPs) settle and are not allowed to infiltrate further down the structure. These pollutant remediation and biodegradation abilities of PPS are well known and documented (Fernández-Barrera, et al., 2010; Newman et al., 2004). A final function was investigated by Coupe, 2004 who found that a biofilm developed on the geotextile fibres and was instrumental in the biodegradation of oil. This has been the subject of many studies eg Pratt et al., 1999; Coupe et al., 2003; Newman et al., 2006 which found that of the oil added to the PPS surface, about 99% is removed, the resultant effluent being relatively hydrocarbon-free (Coupe et al., 2006). In terms of heavy metals and hydrocarbon, studies have found that the effluent water can be of almost potable quality (Bond, 1999; Rodriguez-Hernandez et al., 2010), and certainly has potential for irrigation or other uses where the use of potable quality water is unnecessary (Coupe et al., 2010).

Figure 1 Generalised cross section of a block paver PPS.



With the introduction in the UK of both Future Water in 2008, which changed Permitted Development Rights, such that residents did not have the right to seal their front gardens and also the Flood and Water Management Act, 2010, the use of SUDS is being encouraged. It is likely, therefore, that more SUDS devices, such as PPS will be used as driveways for individual front gardens, or in larger amenity areas. In order to control invasion by weeds, householders and Local Authorities frequently use herbicides; those containing glyphosate (GCH) are amongst the most widely used by Local Authorities for weed control in amenity areas in the UK (RPA, 2011), and it is also intensively used worldwide as a broad-spectrum, non-selective and post-emergence herbicide (Schuster and Gratzfeld-Husgen, 1992). Whilst the former is true for countries such as the UK, USA, Canada and some developing countries, there are European countries such as Denmark, Sweden, the Netherlands and to a certain extent, Germany, which undertake non-chemical weed control as a result of their stricter regulations (Kristoffersen et al., 2008). This study is therefore applicable in those countries where GCH is more widely used.

The efficiency of GCH is enhanced by the addition of a surfactant which may be partially responsible for the compound's relatively high aquatic toxicity (Perkins et al., 2000; Giesy et al., 2000; Tsui and Chu, 2004). Depending on the formulation, and the concentration of glyphosate the product contains, it requires at least a minimum classification of R53 'May cause long term adverse effects in the aquatic environment' (see: http://www.pesticides.gov.uk/guidance/industries/pesticides/topics/pesticide-approvals/pesticides-registration/applicant-guide/updates/Aquatic-Classification-Glyphosate-ppps).

Whilst it is known that GCH is readily broken down in soils by adsorption to particulates and by microbial degradation, there are few studies of the use of dissolved chemicals, such as GCH, on SUDS devices such as PPS and their subsequent ability to carry out their pollution remediation role.

The aims of this study are therefore two-fold:

1. To determine the fate of used engine oil when applied to the surface of a PPS with GCH
2. To determine the fate of PAPs when applied to a PPS surface with GCH

1.1 Methodology

As part of the present study, Mbanaso et al., 2012 investigated the impact of GCH on biofilm associated with PPS test rigs. Three rigs per treatment were used measuring 0.0144 m^2 (30 x 12 x 12 cm) and the 4 treatments were: only oil, only glyphosate, oil and glyphosate and a control where no additions of pollutant were made. Background was further measured on all test rigs before the monitoring experiments began by passing simulated rainfall through them for 89 days before contaminant addition began. This also gave sufficient time for the development of a mature biofilm in the test rigs (Davit, 2010). Figure 2 shows the experimental rig set up.

Figure 2 Experimental set up

1.1.1 Addition of contaminants

Commercially available GCH and used engine oil were the two contaminants used. Based a literature survey, typical oil loadings in urban areas was found to be 9.27 g m^2 year $^{-1}$, which is equivalent to adding pollutants at a rate of 17.8 mg m^2 week $^{-1}$ (Bond, 1999) or 0.12 g week $^{-1}$ taking into account the surface area of the test rigs used. To simulate a worse-case scenario, ten times that amount, or 1.2 g week $^{-1}$ was therefore used. The oil was added randomly to the rig surface using a calibrated pipette before a rainfall event. Approximately 10 ml of proprietary GCH was sprayed onto the rig surface weekly following application of the oil using a trigger gun in 6 separate sprays. The GCH product did not specify any recommended application rate, but the concentration of glyphosate in the formulation was 7.2 g l^{-1}. After GCH application, the rigs were left for 1 hour for it to percolate through the rigs, and rainfall carried out as detailed in the following section.

2.1.2. Simulated rainfall

Based on previous studies utilising simulated rainfall eg Brownstein, 1998; Bond, 1999; Coupe, 2004, a rainfall regime of 15 mm hour^{-1} delivering 13 mm rain in a 52 minute rainfall event was used. In total 250ml of water was applied per rainfall event. To deliver the rain, a plastic bowl, with 2 mm diameter holes drilled at 5 mm intervals was suspended over the rig, 250ml distilled water added which was allowed to drip onto the surface. Whatman 1 filter paper in the base of the bowl enabled even distribution of water across the surface of the rig. Effluent samples were collected from drainage points located at the base of each rig (see Fig 2) two hours after a rainfall event in order to allow a representative sample to drain through.

1.1.2 Analysis

The analyses that were carried out on the effluent are shown in Table 1. Further details can be found in Mbanaso et al., 2012.

Table 1 Monitoring protocol (3 replicates per test rig)

Test model	**Rigs**	**Contaminants**	**Analyses**
1	Oil + GCH	Used oil and glyphosate added on a weekly basis followed by a rainfall event.	• Physical examination: for visible oil sheen, colour, sediment content, cloudiness • Metal concentration: ICP-OES, model Optima 5300DV (Perkin Elmer) (Newman *et al.* 2011) • Hydrocarbon concentration: infra-red spectroscopy (Horiba OCMA 310) (see Coupe 2004) • Turbidity:ELE 430 turbidity meter • pH: Fisherbrand Hydrus 300 pH meter
2	Oil only		
3	GCH only		
4	No oil or GCH		

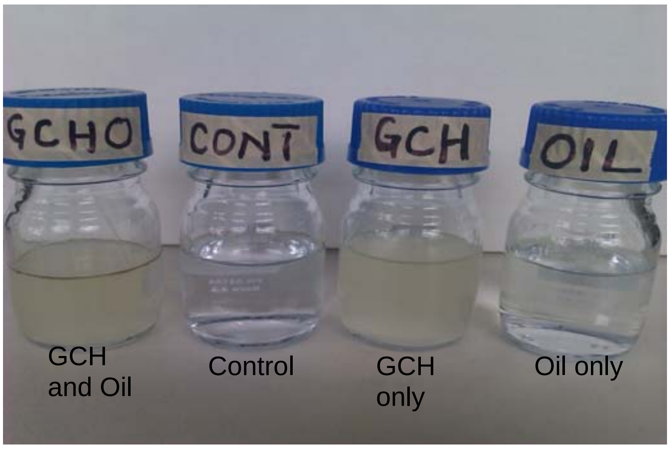
In order to determine the availability of heavy metals in oil, used and new oil were shaken for 30 minutes with either deionised water or GCH and the aqueous supernatant analysed for heavy metals by ICP-OES as indicated above in Table 1. In all cases, 0.3g oil was used and made up to 100ml with deionised water or added to 5ml of 7.2g l^{-1} GCH and made up to 100ml with deionised water. Neat new oil was also analysed for heavy metals.

2. RESULTS

2.1 Physical examination

No oily sheen or sediment was observed in effluent samples from the control rigs or those with just oil added. However, the effluent from rigs with herbicide added was cloudy with an extensive foam as is shown in Fig 3 which was increased by shaking the sample bottles. Furthermore, oil and herbicide rigs were turbid and foamy and the oily sheen became a dark deposit on the side of the sampling bottle.

Figure 2 Examples of effluent samples from the test rigs to illustrate cloudiness in those which have had GCH applied



2.2 *Metal concentration in effluent*

Figs 4a-c show the trends in metals released from the test rigs. Immediately after GCH application, metal concentrations rose above background values, Cu in particular (Fig 4a) exhibits a concentration approximately 100 times that of background. Zinc (Fig 4b) in the control and oil-only rigs was <0.1 mg l^{-1} whereas for those to which GCH and oil were applied and GCH only increased to 1.4 mg l^{-1} and 0.52 mg l^{-1} respectively shortly after the addition of the contaminants. Figure 4c (Pb) exhibits a similar trend since the oil and herbicide rigs recorded the highest concentration of 0.117 mg l^{-1} in comparison with the other rigs. The maximum detected concentration of Pb, Cu and Zn were 0.117, 0.15 and 1.4 mg l^{-1} respectively while WHO, 2011, recommended potable limits are 0.025, 2.0 and 3 mg l^{-1} respectively. Whilst the effluent from a PPS is unlikely to be used for drinking water, nonetheless, the WHO, 2011, potable limits were chosen to compare results against since they were felt to be a best-case scenario for water quality and represent stringent values. The difference between pre- and post contamination concentrations for the herbicide-only and oil and herbicide rigs were found to be statistically significant: $P < 0.05$.

The results of other analysed elements are shown in Table 2. In comparison with WHO 2011 guidelines, some elements were far below the regulatory standards whilst others exceeded the limits.

Table 2 Maximum concentrations of elements in rig effluent obtained over the whole monitoring period.

Rigs	Concentration (mg l^{-1})						
	Al	Ca	Fe	K	Mg	Na	P
Oil and GCH	0.045	38.257	0.463	300.2	2.546	14.107	113.04
Oil only	0.045	10.369	0.037	5.932	0.765	7.748	0.403
Control	0.065	10.798	0.067	12.097	1.157	6.958	0.121
GCH only	0.051	50.82	0.341	351.733	3.197	15.873	152.867
WHO,2011 limits	0.2	ngv	ngv	ngv	ngv	200	ngv

Where: ngv = no guideline value.

2.3 *Hydrocarbon (HC) content of rig effluent*

Figure 5 shows that the highest HC content is found in those rigs to which oil and GCH were applied which reaches 73.2 mg l^{-1} in comparison with 24.5 mg l^{-1} for the herbicide only rigs. It is likely that the surfactant contained in the herbicide formulation contributed to the used oil washing through the rigs and also the herbicides themselves contain hydrocarbons. It is not possible, however, to distinguish between hydrocarbon originating from the herbicides and that in the oil.

Figure 5 Hydrocarbon (HC) in effluent from test rigs

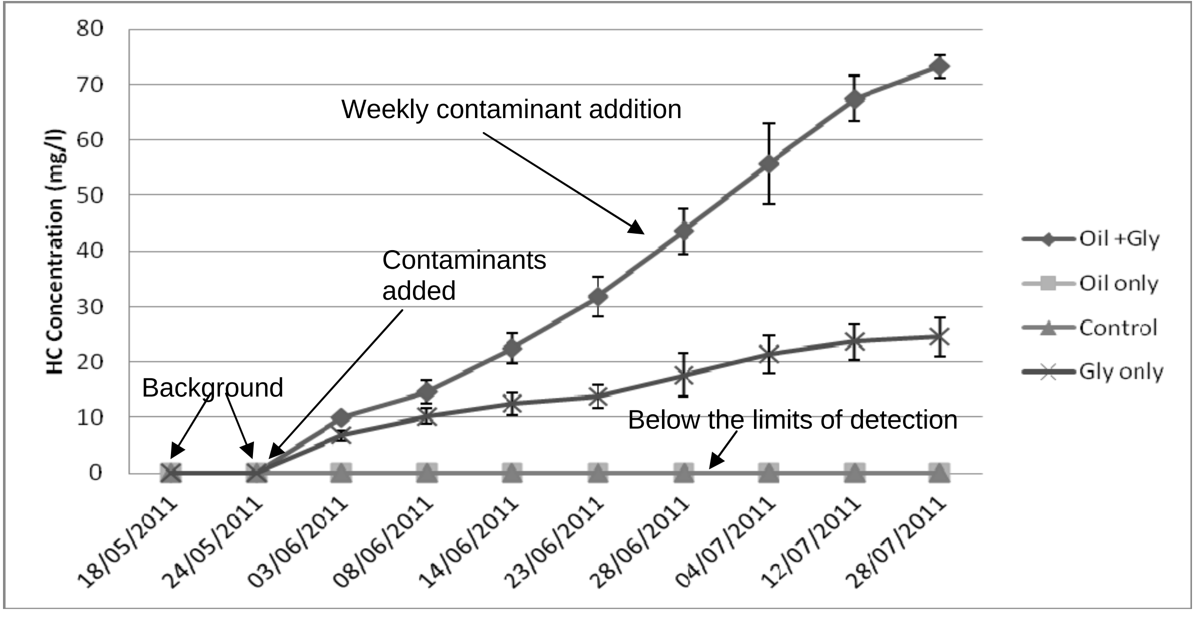
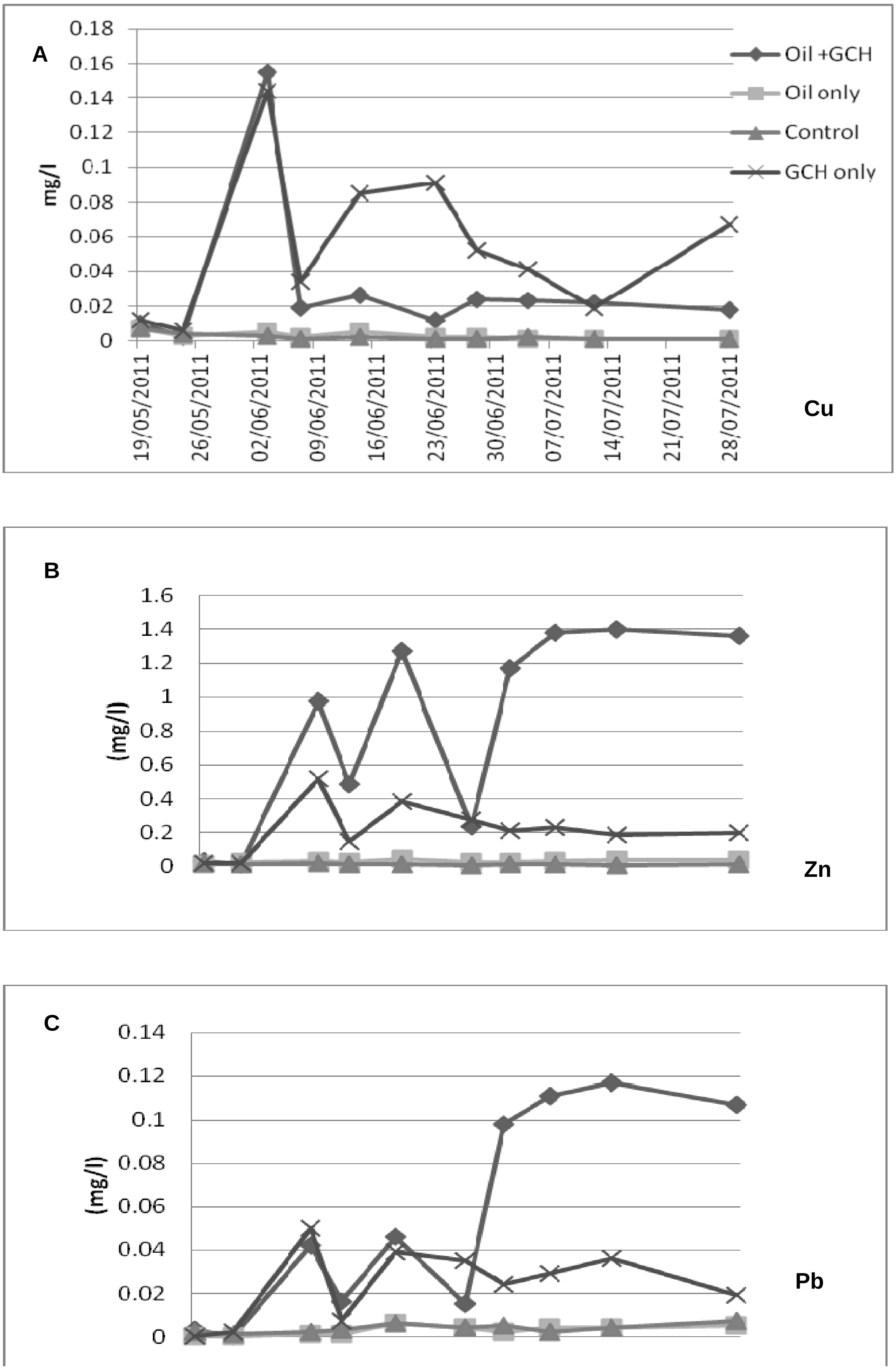


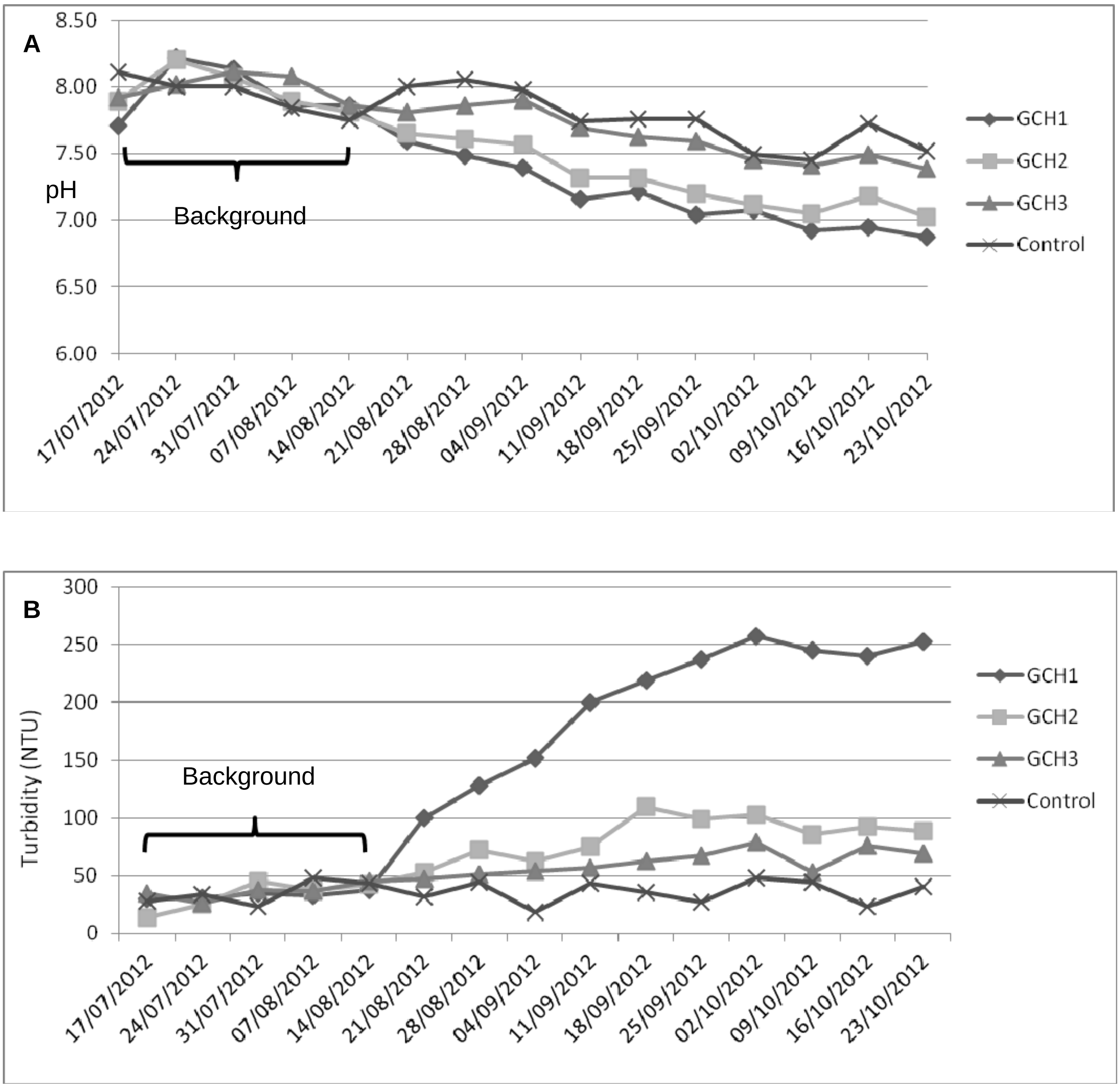
Figure 4 Concentration of metals in effluent from the test rigs a.) Cu b.) Zn c.) Pb



2.4 Turbidity and pH over time in effluent from the test rigs

Figure 6 shows the results of monitoring both pH and turbidity in the effluents from the test rigs. In that these utilise three different concentrations of GCH, they are unlike the testing regime reported in previous sections. However, both indicate similar trends in that the application of the least amount of GCH results in slight divergence from the control, whilst application of the highest concentration leads to a marked difference. This is particularly the case of turbidity where application of 7 200 mg l^{-1} of GCH is reflected in between 3.5 and 2.5 times the turbidity of the other 2 GCH concentrations, and 5 times that of the control. Figure 2 illustrates the difference that could be observed between the rigs which had GCH applied, and those that did not. In the case of pH, the trend for all test rigs is a decline from alkaline values to around neutral for the highest concentration of GCH. Bearing in mind that the aggregates in the test rigs are limestone (see Figs 1 and 2), the background value of about 8 is to be expected, however, all rigs demonstrate a decline of at least half a pH unit.

Figure 6 Trends with time over the monitoring period of: a.) pH. b.) Turbidity



where,
GCH1 = 7200mg l^{-1} glyphosate-containing herbicide
GCH2 = 720mg l^{-1} glyphosate-containing herbicide
GCH3 = 72mg l^{-1} glyphosate-containing herbicide
Control = Oil only

2.5 Dissolution experiments

Table 3 shows the results of the dissolution experiments, clearly illustrating the role that glyphosate plays in the release of metals from oil. Analysis of just the new oil alone shows the concentrations of the metals it contains. By adding deionised water only, very little of the metals are released into solution, but by including GCH into the mixture, particularly Pb and Zn are released in amounts that are close to WHO, 2011 potable limits.

Table 3 rates of dissolution: heavy metals in oil

Solvent	Oil added	Average concentration (mg l^{-1}) n=6			
		Cd	Cu	Pb	Zn
Deionised water	used	0	0	0.004	0.147
	new	0	0	0.003	0.673
Glyphosate	used	0.001	0.008	*0.109	*2.453
	new	0.01	0	*0.08	*2.676
Oil alone	new	1.7	2.0	0.43	300

*close to, or exceeding, WHO, 2011 potable water limits

3. DISCUSSION

3.1 PPS effluent quality

The presence of foaming in the sample bottles from rigs with GCH and GCH plus oil suggests that at least some of the herbicide is not retained in the rig structure, not even on the geotextile. The likely reason is that the rate of adsorption of the herbicide onto the materials in the PPS is lower than that in soil, which tends to tightly bind it onto particles (Pérez et al., 2011). Where PPS is installed and GCH applied, there is potential for herbicide to reach receiving watercourses such as rivers, or down to groundwater. The function of a PPS is to delay the passage of water through it and also to store the water to a certain extent. This delay can be up to several hours but is significantly less than the reported half life of glyphosate of about 4 days (Pérez et al., 2007), therefore it is unlikely that total biodegradation of the herbicide will occur before the water is discharged.

3.2 Oil retention in the PPS

Evidence for the passage of oil through the PPS from those rigs with GCH added was both observational and also analytical. The oily sheen present on the sides of the sampling bottles was supported by increasing HC concentrations when GCH and oil were added to the rigs. This would seem to indicate that the herbicide was involved in the mobilisation of HCs even with geotextiles in place. This is further concern for receiving environments, in particular the potential for groundwater contamination. It is likely that the surfactant present in the GCH formulation may form an emulsion with the oil thus allowing it to pass through the geotextile and the rest of the PPS.

3.3 Metal retention in the PPS

Studies such as that by Wang et al. (2006) suggested that GCH generally increases the mobility of metals in the soil, and this is supported, albeit in PPS rigs, by higher concentrations of Zn, Cu and Pb being found in the effluent from rigs to which herbicide were applied in comparison to those without. The trend of pH is for it to decrease with time, the greater the concentration of applied glyphosate, the greater the decrease in pH. It is well known that a decrease in pH leads to desorption of heavy metals from particulates (Zhou et al., 2004) and hence their release into the effluent. The surfactant in the GCH formulation could also have been involved in the washing of Zn down through the rigs. Therefore, the appearance of both metals and hydrocarbons in effluent from the rigs with oil and GCH suggests that the retention and biodegradation abilities of the PPS were compromised and not functioning properly.

Studies of the interaction between GCH and the aggregates, surface course, geotextiles etc making up a PPS are scarce and need investigation in order to understand their relationships and effects on each other. Such studies would be useful to inform future risk assessments of environmental impacts and would feed into management strategies. Such strategies need to take account of the time it takes for the impacts of herbicides applied to an urban environment to be apparent since there is likely to be a time lag between the application of herbicides and its time of arrival at a water-bearing aquifer. The factors influencing travel times are site specific, depending on land use, soil conditions and depth to the water-table (USGS, 2008). This is particularly of interest to the UK since water-bearing aquifers are mainly permeable and are vulnerable to dissolved contaminants percolating down from the surface (Environment Agency 2011). In-service PPS generally have projected useful lifetimes of 25 years installed in roads, car parks and industrial areas which increases the likelihood of long term contamination. There is therefore an increasing need for better understanding of the connectivity between dissolved pollutants, surface infrastructure and groundwater.

LIST OF REFERENCES

Bond, P.C. (199) *Mineral Oil Biodegradation Within Permeable Pavements: Long-Term Observations.* Unpublished PhD Thesis, Coventry University, Coventry, UK.

Brownstein, J.B. (1998) *An Investigation of the Potential for the Biodegradation of Motor Oil within a Model Permeable Pavement*. Unpublished PhD Thesis, Coventry University, Coventry, UK.

Charlesworth, S. M., Harker, E. and Rickard, S. (2003) *A Review of Sustainable Drainage Systems (SuDS): A soft option for Hard Drainage Questions?* Journal of Geography 88 (2) 99 – 107.

Coupe S. J., E. O. Nnadi and S. Charlesworth (2010) *Multiple Benefits Derived from the Installation of Permeable Pavement Systems.* Proceedings: Novatech, GRAIE, Lyon, France.

Coupe, S.J., (2004) *Oil Biodegradation and Microbial Ecology within Permeable Pavements*. Unpublished PhD Thesis, Coventry University, Coventry, UK.

Coupe, S.J., Smith, H.G., Newman, A.P., Puehmeier, T., (2003) *Biodegradation and microbial diversity within permeable pavements.* European Journal of Protistology. 39, 495–498.

Davit, Y. (2010) *Multiple-scale Analysis of Transport Phenomena in Porous Media*. Unpublished PhD Thesis, Universite de Toulouse, France.

Environment Agency (2011) Aquifers. Available at: http://www.environment-agency.gov.uk/homeandleisure/117020.aspx

Fernández-Barrera, A.H., Castro-Fresno, D., Rodriguez-Hernandez, J., Vega-Zamanillo, A., (2010) *Long-term analysis of clogging and oil bio-degradation in a system of catchment pre-treatment and treatment (SCPT).* Journal of Hazardous Materials. 185, 1221–1227.

Giesy, J.P., Dobson, S., Solomon, K.R., 2000. *Ecotoxicological risk assessment for roundup herbicide*. Rev. Environ. Contam. Toxicol. 167, 35–120.

Kristoffersen P., Rask A. M., Grundy A. C., Franzen I., Kempenaar C., Raisio J., Schroeder H., Spijker J., Verschwele A. and Zarina L. (2008) *A review of pesticide policies and regulations for urban amenity areas in seven European countries*. Weed Research 48, 201–214

Mbanaso, F.U., Coupe S.J, Charlesworth S.M. and Nnadi E.O. (2012) *Laboratory-based experiments to investigate the impact of glyphosate-containing herbicide on pollution attenuation and biodegradation in a model pervious paving system*. Chemosphere. doi.org/10.1016/j.chemosphere.2012.09.058.

Newman, A.P., Coupe, S.J., Smith, H.G., Puehmeier, T., Bond, P. (2006) *The microbiology of permeable Pavements.* In: 8th International Conference on Concrete Block Paving. November 6–8, 2006, California, USA.

Newman, A.P., Puehmeier, T., Kwok, V., Lam, M., Coupe, S.J., Shuttleworth, A., Pratt, C.J. (2004) *Protecting groundwater with oil-retaining pervious pavements: historical perspectives, limitations and recent developments*. Quarterly Journal of Engineering Geology and Hydrogeology. 9, 283–291.

Pérez, G.L., Torremorell, A., Mugni, H., Rodríguez, P., Vera, M.S., Do Nascimento, M., Allende, L., Bustingorry, J., Escaray, R., Ferraro, M., Izaguirre, I., Pizarro, H., Bonetto, C., Morris, D.P., Zagarese, H., (2007) *Effects of the herbicide roundup on freshwater microbial communities: a mesocosm study*. Ecol. Appl. 17, 2310– 2322.

Pérez, G.L., Vera, M.S., Miranda, L.A. (2011) *Effects of herbicide glyphosate and glyphosate-based formulations on aquatic ecosystems*. In: Kortekamp, A. (Ed.), Herbicides and the Environment. In Tech Open, Rijeka, Croatia, pp. 343–368.

Perkins, P.J., Boermans, H.J., Stephenson, G.R., (2000) *Toxicity of glyphosate and triclopyr using the frog embryo teratogensis assay – Xenopus.* J. Environ. Toxicol. Chem. 19, 940–945.

Pratt, C.J., Newman, A.P., Bond, P.C. (1999) *Mineral oil bio-degradation within a permeable pavement: long term observations*. Water Science and Technology. 39, 103– 109.

Rodriguez-Hernandez, J., Fernández-Barrera, A.H., Castro-Fresno, D., Vega-Zamanillo, A., (2010) *Long-term simulation of a system for catchment, pretreatment and treatment (SCPT) of polluted runoff water.* J. Environ. Eng. 136, 1442–1446.

RPA (Risk & Policy Analysts Limited) (2011) *Determining the Usage and Usage Patterns of Amenity Pesticides Across the UK.* Chemicals Regulation Directorate. 240pp.

Schuster, R., Gratzfeld-Husgen, A., (1992) *A Comparison of Pre- and Post-Column Sample Treatment for the Analysis of Glyphosate*. Agilent Technologies, Germany.

Subramaniam, V., Hoggard, P.E., (1988) Metal complexes of glyphosate. J. Agric. Food Chem. 36, 1326–1329.

Tsui, M.T.K., Chu, L.M., 2004. *Comparative toxicity of glyphosatebased herbicides: aqueous and sediment porewater exposures*. Arch. Environ. Contam. Toxicol. 46, 316–323.

Undabeytia, T., Morillo, E., Maqueda, C., (2002) *FTIR study of glyphosate–copper complexes*. J. Agric. Food Chem. 50, 1918–1921.
USGS, (2008) *Pesticides in Groundwater*. Available at: http://ga.water.usgs.gov/edu/pesticidesgw.html
Wang, Y., Zhou, D., Sun, R., Canga, L., Hao, X., (2006) *Cosorption of zinc and glyphosate on two soils with different characteristics.* J. Hazard. Mater. A137, 76–82.
WHO, (2011) Guidelines for Drinking-Water Quality, 4th edition. Available at: http://www.who.int/water_sanitation_health/publications/2011/9789241548151_ch08.pdf
Zhou, D.M., Wang, Y.J., Cang, L., Hao, X.Z., Luo, X.S., (2004) Adsorption and cosorption of cadmium and glyphosate on two soils with different characteristics. Chemosphere 57, 1237–1244.