EQual Paper sludge field trials

LIFE10 ENV/UK/176 Task 6.2

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Executive summary

The EQual LIFE+ programme aims to promote the re-use and recycling of waste materials whilst protecting human health and the environment. Deriving value from waste materials by turning them back into safe, high quality products is an essential element in the move towards a more circular economy. Offering both economic and environmental benefits, if supported and regulated appropriately, waste-derived products improve business resource efficiency and competitiveness, reduce reliance on landfill, and help to conserve virgin raw materials. The Environment Agency is leading the programme with six partners.

As part of the EQual programme, field trials for four waste derived materials were undertaken to improve understanding of the behaviour of these materials in the environment. The evidence base obtained from the trials will support the appropriate use of these materials in place of non-waste materials. Two of the field trials focus on the construction industry (pulverised fuel ash and incinerator bottom ash aggregate), and two on agricultural use (poultry litter ash and paper sludge).

This report provides details and results from the paper sludge (PS) field trials, which aimed to further understanding of the environmental (soil, terrestrial organisms and controlled waters) and human health risks of land application of paper sludge (PS) to agricultural soils. The field trials were carried out by ADAS UK Ltd and Harper Adams University College.

The objectives of the field trials were to:

1. assess the environmental impacts of the application of PS to agricultural soils;
2. provide data to inform future generic Quantitative Risk Assessment (QRA); and
3. improve understanding of the magnitude of agricultural benefits derived from PS compared to non-waste-derived alternatives*.

*Objectives 1 and 2 were the primary objectives of the field trials.

The research was undertaken at two existing experimental sites that had received repeated additions of PS as part of previous Defra-funded research (termed the 'historic PS' treatment). The sites were Harper Adams in Shropshire and Gleadthorpe in Nottinghamshire; both on light textured soils (6-12% clay). As well as the historic PS treatment, there was an untreated control and fresh PS treatment, each replicated three times. Fresh PS was applied at a rate of 30 t/ha (fresh weight) to new plots established in Autumn 2013; there were no additions of PS to the historic PS treatment. Spring barley and winter wheat were grown at Gleadthorpe for harvests 2013 and 2014, respectively. At Harper Adams, winter wheat was grown in 2013, and spring barley in 2014. Topsoil (0-15cm) sampling was undertaken in January 2013 on historic PS and control treatments, and in April 2014 on the fresh PS and control treatments.

There was a small (*c.*0.3-0.6 pH units), but not statistically significant ($P>0.05$) increase in topsoil pH *c.*6 months following the addition of fresh PS material, relative to the untreated control. However, overall, a single 30 t/ha application of PS had very little effect on topsoil chemical properties, microbial biomass and aggregate stability, with no consistent change over the 6 month period. This was not surprising as it has been shown that repeated and relatively large organic material additions are needed to produce measurable changes in soil properties.

However, the historic PS treatment plots in comparison to the untreated control, provided valuable information on the longer-term effects of repeated PS additions. Here 6 to 9 years of annual applications at rates varying between 30 and 75 t/ha (fresh weight) and supplying up to 32 t/ha C, resulted in a clear demonstration of the value of PS as a liming material as well as a soil conditioner. Topsoil pH had increased to c.pH7.8 at both sites, relative to the untreated control at

pH 5.7-6.0, and topsoil total C contents increased by 25-40% resulting in an extra 6-8 t/ha C in the topsoil relative to the untreated control. There was very little effect of the repeated PS additions on topsoil metal concentrations, consistent with previous work that suggested the impact of heavy metal additions on human and animal health following PS addition was very low.

The yield of winter wheat and spring barley increased by c.1.4 t/ha and c.0.2 t/ha following fresh PS treatment at Gleadthorpe and Harper Adams respectively, which although not significant statistically, most likely reflected the additional manufactured fertiliser N that was applied to the fresh PS treatment to counter for potential N immobilisation following the PS additions.

An additional replicated study evaluating the effect of storage (over a c.12 month period) on the properties of PS was established in August 2013. The volume and chemical composition of leachate draining from the heaps was determined over the 12 month period, together with any changes in the composition of the PS material. Over the storage period the total weight of PS material within each heap decreased by c.25%, equivalent to a loss of c.1.25 t. This was most likely due to decomposition (oxidation) of the organic fraction of the PS material, and was associated with a decrease in both the total carbon and organic matter content.

Although there was some variability in composition of the PS material over the c.12month period, the only consistent variation was for total carbon/organic matter which decreased by up to 25%, total sulphur, which decreased to negligible concentrations by the end of storage, and total manganese and strontium concentrations which increased by 10-15%. E.coli was present at the start of the storage period, possibly due to the presence of some biologically treated material within the batch of PS, but after just 1 month of storage these had died off.

Over the storage period the PS heaps did generate leachate containing elevated concentrations of multiple pollutants (e.g. nitrate-N, ammonium-N and phosphorus-P, with BOD and E-coli elevated in the first month of storage), which could cause detrimental effects if they reached surface water bodies in an undiluted form. This demonstrates the need to follow good agricultural practice for the storage of PS in temporary field heaps, and in particular, the Confederation of Paper Industries Code of Practice. It should be noted however, that total loadings were low and well below (i.e. less than a tenth) those measured from solid manure heaps (in particular nitrogen/nitrate, phosphorus, BOD and E-coli). In practice pollutants in leachates infiltrating soil underneath a field heap of PS or in runoff from the heap are likely to either be retained in the soil or will be diluted with runoff from the rest of the field.

The PS field trials demonstrated no significant negative effect on a range of soil chemical, physical and biological properties or on the uptake of potential substances of concern by cereal crops, . This suggests that a single application of PS to agricultural soils presented no unacceptable environmental or human health risks. However, further work over longer time periods and higher application rates would be required in order to fully understand any potential risks. Here, the study benefitted from the historic PS treatment plots which had received repeated application of PS over several years and provided a useful dataset. Together with the earlier sampling undertaken as part of the SOIL-QC experimental programme, this demonstrated the agricultural benefit of PS as a liming material and soil conditioner leading to an increase in topsoil organic matter and improved soil biological functioning. However, it is important that adequate manufactured fertiliser N is applied in order to account for potential N immobilisation following PS application so that crops do not become N-limited and yields are not impaired.

The PS field trials furthered understanding of the environmental impact and agricultural benefits of the application of PS to agricultural soils. The study also highlighted the importance of following good practice when storing PS materials in temporary field heaps in order to avoid potentially harmful leachate reaching surface water bodies in an undiluted form. The results from this study will be useful for informing future QRAs on the storage and land-spreading of PS. The objectives for the EQual PS field trials have therefore been achieved.

Contents

1. Background

In the United Kingdom millions of tonnes of biodegradable organic materials are landfilled every year. By diverting organic materials away from landfill they are available to be beneficially recycled to land. This has the potential to provide benefits in terms of the sustainable use of plant nutrients reducing the need for manufactured fertilisers, quarried lime and the addition of organic matter to improve soil structural condition. However it is essential that the application of organic wastes to land is truly beneficial and is not harmful to the environment (i.e. soil, water and air quality) or human health.

The EQual LIFE+ programme aims to promote the re-use and recycling of waste materials whilst protecting human health and the environment. Deriving value from waste materials by turning them into safe, high quality products is an essential element in the move towards a more circular economy. Offering both economic and environmental benefits, if supported and regulated appropriately, waste-derived products improve business resource efficiency and competitiveness, reduce reliance on landfill, and help to conserve virgin raw materials.

The Environment Agency is leading the programme with six partners: Rijkswaterstaat (the Netherlands' Ministry of Infrastructure and the Environment), The Chartered Institution of Wastes management, Organics Recycling Group Environmental Services Association, Northern Ireland Environment Agency and Energy UK.

As part of the EQual programme field trials for four waste derived materials were undertaken to improve understanding of the behaviour of these materials in the environment. The evidence base obtained from the trials will support the appropriate use of these materials in place of non-waste materials.

Two of the field trials focus on the construction industry (pulverised fuel ash and incinerator bottom ash aggregate), and two on agricultural use (poultry litter ash and paper sludge). This document reports the paper sludge field trials. The field trials were carried out by ADAS UK Ltd and Harper Adams University College.

1.1. Paper sludge (PS) field trials

Over the period 2005-2010 an average of c.800,000 tonnes (fresh weight) of PS was applied to agricultural land, equivalent to c.60% of the total PS produced (EA, 2012). Whilst there has been some work assessing agricultural benefit, limited work has been carried out on the impact of applications to the wider environment (i.e. water, crop and soil quality) and human health.

Field trials were carried out to further understanding of the environmental (soil, terrestrial organisms and controlled waters) and human health risks of land application of PS to agricultural soils compared with non-waste-derived alternatives.

1.2. Aims and Objectives

The aims of the field trials were to:

1. assess the environmental impacts of the application of PS to agricultural soils;
2. provide data to inform future generic Quantitative Risk Assessment (QRA); and
3. improve understanding of the magnitude of agricultural benefits derived from PS compared to non-waste-derived alternatives*.

Aims 1 and 2 were the primary objectives of the field trials.
*Subsequent QRA does not form part of this project.

The objectives of the field trials were to answer the following specific research questions:

1. With respect to specific determinands (Section 2), how do physical and chemical properties of soil and pore water change over time in:
   a. Control plots
   b. Plots with application of paper sludge ?
2. How do physical and chemical properties of soil and pore water in plots with application of paper sludge compare to control plots?
3. To what extent are potential chemicals of concern (PCOCs) taken up by crops grown with application of paper sludge?
4. How does uptake of PCOCs by crops grown with application of paper sludge compare to uptake by crops grown in control plots?
5. How does the total soil microbial biomass change over time in soils with application of paper sludge?
6. How does the total soil microbial biomass in soils with application of paper sludge compare with total soil microbial biomass in control plots?
7. How do storage durations affect key properties of the paper sludge (e.g. nutrient content, pH, pathogens)?
8. How do the yields of crops grown with application of paper sludge compare with those grown in control plots?

2. Methodology

2.1. Field trials sites

The research was undertaken at two existing experimental sites at Harper Adams University (sandy loam textured soil) and ADAS Gleadthorpe (loamy sand textured soil) (Figure 2.1). The sites previously received repeated applications of PS as part of the Defra SOIL-QC experimental programme (SP0530, Defra, 2011), Table 2.1. These repeated PS applications are termed the 'historic PS' treatment for the purposes of this study.

a) Harper Adams prior to drilling; March 2014

b) Gleadthorpe – spring barley; June 2013

Figure 2.1. Experimental sites

Table 2.1 Experimental sites

Site	Soil properties[1]			Cropping rotation[2]		Number of annual PS additions[3]	Date PS last applied[4]
	Texture	Organic matter (%)	Bulk density (g/cm^3)	2012/13	2013/14		
1. Harper Adams	Sandy loam (12% clay)	2.7	1.23	WW	SB	9	September 2012
2. Gleadthorpe	Loamy sand (6% clay)	2.4	1.42	SB	WW	6	March 2010

[1]Topsoil properties measured in 2001 (Bhogal *et al.,* 2009)
[2]WW = Winter wheat; SB = Spring barley
[3] PS was applied annually at rates ranging between 30 and 75 t/ha/yr FW ('Historic PS' treatment)
[4]Date PS was last applied to the historic treatment

2.2. Experimental treatments and design

The experiment comprised a control treatment (i.e. manufactured fertiliser applied following the recommendations in the "Fertiliser Manual (RB209)" (Defra, 2010) and FACTS qualified advice) and a PS treatment (termed the 'fresh PS' treatment), applied at an agronomically justified rate of 30 t/ha fresh weight.

Each treatment (including the control) was replicated three times and arranged in a randomised block design at Harper Adams and fully randomised design at Gleadthorpe Figure 2.2). Plots were 6 x 10m at Harper Adams and 5 x 15m at Gleadthorpe. No other organic materials had been

applied previously to these plots, which were embedded within a pre-existing experimental layout that included the historic PS treatment at each site, as described below.

a) Harper Adams (randomised blocks) – treatments discussed in this report are highlighted in grey

Block 1	*Block 2*	*Block 3*
Historic PS	PLA	Fresh PS
Control	Fresh PS	Historic PS
PLA	P & K	Control
Fresh PS	Control	P & K
P & K	Historic PS	PLA

b) Gleadthorpe (fully randomised) – treatments discussed in this report are highlighted in grey

Fresh PS	P & K	PLA	P & K	Historic PS	Control
Fresh PS	PLA	P & K	PLA	Control	
	Fresh PS	Historic PS	Control	Historic PS	

*note: the fresh PS treatments were embedded within a pre-existing experimental layout

Figure 2.2 Schematic of the experimental layout at each site

Historic PS plots

The original intention of the research was to make use of the existing PS treatment, in order to provide robust scientific evidence on the environmental risks of repeated PS additions, which could not be achieved/measured following a single application alone. However, baseline sampling showed that the pH of the existing plots was above the level at which application of paper sludge was agronomically justifiable. Therefore it was necessary to establish fresh plots. This meant the historic PS treatment was only sampled as part of the site characterisation sampling programme (detailed below) and 'fresh PS' treatment plots were established in Autumn 2013 as it was too late to establish a new treatment for the 2013 crop harvest.

2.3. Site characterisation ('baseline') sampling

Topsoil (0-15cm depth) samples were taken in January 2013 from the control and historic PS treatment plots in order to characterise the soils. Separate site characterisation samples were taken from the control and fresh PS treatment plots in September 2013. Samples were taken using a hand-held corer and comprised of *c*.20 cores taken at intervals across each plot and bulked together to give a single soil sample from each plot (see Appendix 1: method statement for baseline soil sampling). Table 2.2 details the analyses undertaken on each of the soil samples.

Table 2.2 Topsoil analysis suite

Property
Total Al, Sb, As, Ba, Be, B, Cd, Ca, Cr, Co, Cu, Fe, Pb, Li, Mg, Mn, Hg, Mo, Ni, P, K, Se, Ag, Na, Sr, Tl, Sn, Ti, V and Zn
Hexavalent Cr
pH
Olsen extractable P
Ammonium nitrate extractable K & Mg
Organic C, total N and C:N ratio
Organic matter
Mineral N (ammonium-N & nitrate-N)
Electrical conductivity
E-coli[1]
Microbial biomass C and N
Aggregate stability

[1]E-coli only determined on the Fresh PS and control treatments at site characterisation in August 2013 and *c*.6 months following PS application in April 2014.

Additional topsoil (0-15cm) samples were taken for the determination of soil microbial biomass carbon (C) and nitrogen (N), using the chloroform incubation methodology (see Appendix 1: method statement for microbial biomass analysis; Jenkinson & Powlson, 1976), and aggregate stability using the dispersion ratio method on 5-30mm soil aggregates (see Appendix 1: method statement for aggregate stability; Anon, 1982).

The original proposal also intended to analyse the pore water extracted from the soil, however, even though the samples were taken when the soils were at or close to field capacity, insufficient pore water could be extracted for any meaningful analyses to be performed. This was because the water retention capacity of sandy soils is very low.

2.4. Material application

The topsoil pH of the plots designated for the *fresh* PS application was *c*.5.9 at Gleadthorpe and 6.0 at Harper Adams. Therefore, these plots had a lime requirement of *c.*10 t/ha to bring the soil up to the optimum pH for arable rotations of 6.5 (Defra, 2010) and maintain it across the rotation (assuming a 1 t/ha/yr lime loss rate and four course rotation). The analysis supplied with the PS reported a total neutralising value (TNV) of 32% on a dry weight basis (70% dry matter). A 30 t/ha application of this PS would therefore apply the equivalent of 12 tonnes of ground limestone/chalk (*c.*50%TNV), as required. This was applied to the fresh PS treatment plots in Autumn 2013.

It should be noted that the dry matter and TNV of the supplied PS was considerably higher than average reported values of 32% dry matter and 12% TNV for pulp and paper sludge (EA, 2012). The application rate of 30 t/ha is therefore at the lower end of 'typical' application rates, which range from 30-200 t/ha (fresh weight) for non-biologically treated sludges and from 25-65 t/ha for biologically treated sludges (Gibbs *et al*., 2005). *Note:* the supplied PS material was predominantly de-inking sludge (non-biologically treated) with *c*.2% biological sludge[1].

The control plots received recommended rates of manufactured fertiliser nutrients based on the “Fertiliser Manual (RB209)” (Defra, 2010) and FACTS qualified advice. In order to minimise potential confounding interactions, all treatment plots (including the control) had manufactured fertilisers applied (based on “Fertiliser Manual (RB209)” recommendations) to ensure as far as was practically possible that no major nutrient limited plant growth.

At Gleadthorpe this included the application of 5 t/ha lime to all of the plots as the pH across the site was *c.*6.0 in December 2012 ahead of the planting of spring barley, a crop sensitive to soil acidity (MAFF, 1983). In the case of the PS additions in Autumn 2013, additional manufactured fertiliser N was applied in Spring 2014 to account for N lock up. See Appendix 2 for a full diary of activities at the experimental sites including the dates and rates of all manufactured fertiliser applications.

The PS material was applied by hand (Figure 2.3) (method statement in Appendix 1). Following application the PS was incorporated by ploughing at Gleadthorpe (plough depth: *c*.20cm) and by disc at Harper Adams (to a depth of *c*.15cm). Material was stored and used in accordance with the CPI Code of Good Practice for Landspreading of Paper Mill Sludges (CPI, 2011). A Regulatory Position Statement was obtained from the EA for the use of the PS materials.

[1] Rachel Bain, personal communication

Figure 2.3 . Experimental plot following PS application

Analysis of the applied materials

Samples of archived PS materials as applied to the historic PS treatment at Gleadthorpe (1 sample) and Harper Adams (4 samples, comprising of 3 samples of the material applied in 2012 and one archived historic sample) were analysed in Spring 2013. Samples of the fresh applied at each site were analysed in Autumn 2013. Table 2.3 Paper sludge analysis suite

details the analyses undertaken on the applied materials.

Table 2.3 Paper sludge analysis suite

Property
Dry matter & pH
Total Al, Sb, As, Ba, Be, B, Cd, Ca, Cr, Co, Cu, Fe, Pb, Li, Mg, Mn, Hg, Mo, Ni, P, K, Se, Ag, Na, Sr, Tl, Sn, Ti, V and Zn
Hexavalent Cr
Total N & S
Organic carbon & C:N ratio
Electrical conductivity
Total neutralising value (TNV)
E-coli[1]

[1]E-coli was only determined on the Fresh PS material.

2.5. Soil sampling and analysis

Topsoil samples (0-15cm) were taken from the control and fresh PS treatment plots in April 2014, *c*.6 months after treatment application. *Note:* the historic PS treatment plots were only sampled at site characterisation in January 2013. Samples were taken from each plot (see method statement for annual soil sampling; Appendix 1) and transported to National Laboratory Service (NLS) for the analyses detailed in Table 2.2. As at site characterisation, the original proposal intended to analyse the pore water extracted from the soil, however, even though samples were taken when the soil was close to field capacity, water retention on these sandy soils is very low and insufficient pore water could be extracted for any meaningful analyses to be performed.

Additional soil samples were taken for the determination of soil microbial biomass C and N, using the chloroform incubation methodology (Jenkinson & Powlson, 1976), and aggregate stability using

the dispersion ratio method on 5-30mm soil aggregates (Anon, 1982), as detailed above and in Appendix 1.

2.6. Crop yields and grain analysis

Crop yields were determined in August 2014 at both sites using a plot combine (see method statement for grain yield and analysis; Appendix 1), with samples of the grain analysed for total Al, Sb, As, Ba, Be, B, Cd, Ca, Cr, Co, Cu, Fe, Pb, Li, Mg, Mn, Hg, Mo, Ni, P, K, Se, Ag, Na, Sr, Tl, Sn, Ti, V and Zn.

2.7. Storage study

The storage study was set up in August 2013 at Gleadthorpe. Three replicate field heaps of fresh PS material (as used in the field experiment) were constructed in a series of hydrologically isolated, sloping concrete bunkers. Each heap comprised *c.*5 tonnes of fresh PS material (Figure 2.4). Leachate from each heap was collected at the lowest corner of the bunkers using a short length of perforated plastic drainage pipe to direct the leachate into three individual collection tanks.

During construction of the heaps triplicate samples were taken for analysis and four 'litter' bags, each containing *c.*2kg of the PS material, were buried at known separate locations within each heap. These were retrieved after approximately 1, 3 and 6 months and at the end of the storage period (*c.*12 months) and analysed as detailed in Table 2.3.

Measurements of the quantity of leachate from each storage heap were taken and related to rainfall volumes. Samples were taken from the collection tanks on a monthly basis and analysed for total N, ammonium-N, nitrate-N, Total P, orthophosphate-P, BOD, pH, e-coli, Total Al, Active Al, Sb, As, Ba, Be, Cd, Cr, hexavalent Cr, Co, Cu, Fe, Pb, Mn, Hg, Mo, Ni, Se, Ag, Te, Tl, Sn, Ti, U, V and Zn. See Appendix 3 for a detailed method statement covering the storage study.

Figure 2.4 Construction of the PS storage heaps

2.8. Statistical analysis

The results from the field study were analysed using two sample T Tests using Genstat version 12 (VSN International Ltd, 2010) to ascertain whether there were any statistically significant (P<0.05) effects of the PS additions relative to the untreated control plots on the soil chemical, biological and physical properties, crop yields and uptake of PCOCs. Changes in soil properties over the 6 months between site characterisation and topsoil sampling in April 2014 were evaluated using conventional analysis of variance (ANOVA), with time and treatment as factors. Changes in selected soil properties on the historic PS treatment plots between the final sampling undertaken as part of the SOIL-QC experimental programme in 2006/7 (Defra, 2011) and the EQual sampling in 2013 were evaluated using ANOVA (with time and treatment as factors).

Potential changes in the composition of stored PS and its leachate during the *c*.12 month storage period were evaluated using both ANOVA, to determine whether there were any statistically significant changes over time (P<0.05), and regression, to determine the magnitude and direction of any changes in composition, using Genstat Version 12 software.

3. Results

3.1. Site baseline characterisation

Characterisation of the fresh PS and control treatment plots was undertaken in September 2013 prior to treatment application in order to determine the baseline against which to assess the results (Table 3.1).

At Gleadthorpe, the only significant (P<0.05) background variation prior to treatment application was in topsoil extractable magnesium, which was higher on the untreated control compared to the untreated PS treatment plots. At Harper Adams total and extractable potassium and extractable phosphorus were higher (P<0.05) on the untreated PS plots compared to the untreated control. This background variation will be taken into account when considering the results of the topsoil sampling undertaken c.6 months after fresh PS additions.

Table 3.1 Site characterisation soil chemical parameters (treatment means), September 2013

Determinand	Unit	Gleadthorpe			Harper Adams		
		Control	Fresh PS*	P statistic[1]	Control	Fresh PS*	P statistic[1]
Nitrogen	% dm	0.08	0.08	*NS (0.87)*	0.18	0.19	*NS (0.29)*
Ammoniacal_N	mg/kg dm	<2	<2	*NS (1.0)*	<3	<2	*NS (1.0)*
Nitrate nitrogen	mg/kg dm	<3	<3	*NS (1.0)*	12.4	12.8	*NS (0.93)*
Total carbon	% dm	1.00	1.07	*NS (0.45)*	1.52	1.58	*NS (0.71)*
Organic matter	% dm	1.83	1.97	*NS (0.79)*	2.60	2.90	*NS (0.42)*
C:N ratio	ratio	13	13	*NS (0.79)*	8	8	*NS (0.70)*
Conductivity	µs/cm	1997	2010	*NS (0.12)*	2060	2063	*NS (0.82)*
pH	unit	6.7	6.8	*NS (0.79)*	6.8	6.5	*NS (0.52)*
Extractable P	mg/l	38.8	41.9[2]	*NS (0.70)*	66.7	100.2	***<0.001***
Extractable K	mg/l	65.8	77.2	*NS (0.07)*	125.0	179.7	***0.02***
Extractable Mg	mg/l	67.3	42.3	***0.006***	47.3	45.0	*NS (0.57)*
Aluminium	mg/kg dm	4707	4997	*NS (0.33)*	10867	11133	*NS (0.55)*
Antimony	mg/kg dm	<1	<1	*NS (1.0)*	<1	<1	*NS (1.0)*
Arsenic	mg/kg dm	4.33	4.39	*NS (0.77)*	6.32	6.52	*NS (0.36)*
Barium	mg/kg dm	23.1	23.7	*NS (0.52)*	61.2	61.8	*NS (0.80)*
Beryllium	mg/kg dm	0.31	0.34	*NS (0.21)*	0.51	0.52	*NS (0.61)*
Boron	mg/kg dm	2.61	2.59	*NS (0.98)*	7.28	7.43	*NS (0.80)*
Cadmium	mg/kg dm	<0.2	<0.2	*NS (1.0)*	<0.2	<0.2	*NS (1.0)*
Calcium	mg/kg dm	1273	1529	*NS (0.55)*	2533	2483	*NS (0.89)*
Chromium	mg/kg dm	6.55	6.65	*NS (0.69)*	13.8	14.2	*NS (0.64)*
Chromium VI	mg/kg dm	<0.6	<0.6	*NS (1.0)*	<0.6	<0.6	*NS (1.0)*
Cobalt	mg/kg dm	1.74	1.83	*NS (0.30)*	3.90	4.19	*NS (0.33)*
Copper	mg/kg dm	4.62	4.92	*NS (0.35)*	13.4	13.9	*NS (0.42)*
Iron	mg/kg dm	7743	7487	*NS (0.22)*	11733	11733	*NS (1.0)*
Lead	mg/kg dm	15.5	15.3	*NS (0.77)*	19.4	18.9	*NS (0.66)*
Lithium	mg/kg dm	6.00	6.85	*NS (0.16)*	14.3	15.1	*NS (0.51)*
Magnesium	mg/kg dm	696	809	*NS (0.38)*	2410	2527	*NS (0.44)*
Manganese	mg/kg dm	186	155	*NS (0.14)*	277	298	*NS (0.48)*
Mercury	mg/kg dm	<0.2	<0.2	*NS (1.0)*	<0.2	<0.2	*NS (1.0)*
Molybdenum	mg/kg dm	<1	<1	*NS (1.0)*	<1	<1	*NS (1.0)*

Nickel	mg/kg dm	3.88	4.28	*NS (0.30)*	10.2	10.5	*NS (0.66)*
Phosphorus	mg/kg dm	582	583	*NS (0.99)*	1107	1203	*NS (0.31)*
Potassium	mg/kg dm	694	730	*NS (0.42)*	2207	2357	***0.05***
Selenium	mg/kg dm	<1	<1	*NS (1.0)*	<1	<1	*NS (1.0)*
Silver	mg/kg dm	<1	<1	*NS (1.0)*	<1	<1	*NS (1.0)*
Sodium	mg/kg dm	25.7	28.2	*NS (0.50)*	62.0	64.3	*NS (0.67)*
Strontium	mg/kg dm	4.64	5.46	*NS (0.22)*	9.18	9.30	*NS (0.83)*
Thallium	mg/kg dm	<1	<1	*NS (1.0)*	<1	<1	*NS (1.0)*
Tin	mg/kg dm	1.04	1.09	*NS (0.14)*	1.34	1.35	*NS (0.74)*
Titanium	mg/kg dm	74.1	73.7	*NS (0.92)*	107	110	*NS (0.67)*
Vanadium	mg/kg dm	10.2	10.1	*NS (0.78)*	17.7	18.2	*NS (0.54)*
Zinc	mg/kg dm	25.9	25.5	*NS (0.85)*	63.4	64.2	*NS (0.75)*
E-coli (confirmed)	No/g	<9	<9	*NS (1.0)*	<10	<9	*NS (1.0)*
Biomass C	mg/kg	81	70	*NS (0.56)*	157	158	*NS (0.97)*
Biomass N	mg/kg	16	14	*NS (0.61)*	25	26	*NS (0.61)*
Agg stability[3]	% w/w	10	10	*NS (0.83)*	*6.2*	6.9	*NS (0.55)*

*Note soil samples were taken prior to fresh PS application;

[1]Statistical analysis undertaken using a t test; NS = not significant (*P*>0.05); numbers in brackets indicate the P statistic;

[2]Mean of 2 replicate plots;

[3]Aggregate stability measured by the dispersion ratio (ratio of silt and clay suspended by mild slaking forces expressed as a % of the total silt and clay content); Ratios in the range 6-10% suggest the soil is 'stable', 11-15% indicate that the soil is 'fairly stable', while ratios in the range 16-25% suggest the soil is 'somewhat unstable' (Anon, 1982).

3.2. Composition of the applied materials

The fresh PS material had a higher dry matter (*c*.75%) but lower TNV (*c*.23%) than the historic archived PS materials (at 62% DM and 37% TNV; Table 3.2). However these were all considerably higher than the average reported values of 32% dry matter and 12% TNV for pulp and paper sludge (EA, 2012). The TNV of the fresh PS material analysed post-spreading was lower than the reported TNV value that was supplied with the material (i.e. 32% TNV). This meant the fresh PS material supplied the equivalent of *c*.10 t/ha lime instead of the calculated 12 t/ha.

The total C content of the fresh PS was also higher than the historic PS materials which, together with a lower total N content, resulted in a higher C:N ratio at *c.*55:1. However this was still within the range of reported values for pulp and paper sludges (which ranged from 12:1 – 200:1; EA, 2012). In general biologically treated paper sludges have a higher available N content and lower C:N ratio than chemically/physically treated materials (Gibbs *et al.,* 2005) and do not usually result in N lock-up following land spreading (Defra, 2010). The fresh PS material was largely de-inking sludge (non-biologically treated), whereas the historic PS was predominantly secondary biologically treated sludge.

The C:N ratio is not an accurate guide to potential N lock up following land spreading (Gibbs *et al.,* 2005). However in general *c*.0.8 kg of inorganic N is required per tonne (fresh weight) of chemically/physically treated PS applied (Defra, 2010). At 18.5%C the single application of fresh PS (at 30 t/ha fresh weight) supplied *c.* 4 t/ha carbon.

The total metal content of the fresh and historic PS applications were within the range of reported values for pulp and paper sludges (EA, 2012). Although it was not possible to statistically analyse the differences in composition of the archived and fresh PS samples, due to lack of replication, the fresh PS had numerically higher concentrations of total Al, Ba, Cr, Cu and Na, compared to the archived materials, but lower concentrations of Fe and Zn. This is most likely due to the difference sources (paper mills) and secondary processing of the PS materials.

Table 3.2 Composition of the fresh and historic PS additions

Determinand	Unit	Gleadthorpe		Harper Adams		
		Archived PS[1]	Fresh PS[2]	Archived PS[1]	Historic PS[3]	Fresh PS[2]
Dry matter - DM	%	64.8	76.2	60.3	60.8	72.3
pH	unit	7.66	7.87	7.86	7.88	7.82
TNV	% dw	37.6	24.7	37.6	37.7	22.0
Conductivity	µS/cm	1380	601	633	578	624
LOI	% dm	15.6	22.0	14.9	14.7	20.6
Organic matter	% dm	13.0	19.0	14.0	13.3	18.3
Total carbon	% dm	16.3	18.5	15.5	15.1	18.5
C:N ratio	ratio	31.7	55.3	33.8	34.9	55.9
Total nitrogen	kg/t fw	3.34	2.61	2.76	2.66	2.40
Phosphate (P_2O_5)	kg/t fw	1.09	0.63	0.99	0.96	1.12
Potash (K_2O)	kg/t fw	0.28	0.33	0.23	0.21	0.70
Magnesium (MgO)	kg/t fw	2.23	3.41	2.07	2.04	3.78
Sulphur (SO_3)	kg/t fw	0.01	<0.02	0.01	0.01	<0.02
Calcium	kg/t fw	186	182	163	167	179
Aluminium	mg/kg dm	3420	5540	3060	3013	5783
Antimony	mg/kg dm	<1.00	<1	2.03	1.57	<1
Arsenic	mg/kg dm	0.67	0.79	1.30	1.01	0.91
Barium	mg/kg dm	55.8	74.5	59.0	57.3	77.6
Beryllium	mg/kg dm	<0.1	0.10	<0.1	<0.1	0.12
Boron	mg/kg dm	1.81	2.65	1.47	1.73	3.46
Cadmium	mg/kg dm	<0.2	<0.2	<0.2	<0.2	<0.2
Chromium	mg/kg dm	5.35	12.6	5.2	5.16	13.3
Chromium VI	mg/kg dm	<0.3	<0.6	<0.3	<0.3	<0.6
Cobalt	mg/kg dm	1.73	1.16	1.80	1.75	1.21
Copper	mg/kg dm	34.2	158	33.9	34.6	164
Iron	mg/kg dm	2350	836	2470	2380	891
Lead	mg/kg dm	2.94	7.96	6.29	4.87	8.51
Lithium	mg/kg dm	5.96	12.2	6.16	5.71	13.3
Manganese	mg/kg dm	100	100	99.1	97.9	110
Mercury	mg/kg dm	<0.2	<0.2	<0.2	<0.2	<0.2
Molybdenum	mg/kg dm	1.84	<1	1.55	1.55	1.03
Nickel	mg/kg dm	2.77	4.02	2.75	2.75	4.11
Selenium	mg/kg dm	<1.0	<1	<1.0	<1.0	<1
Silver	mg/kg dm	<1.0	<1	<1.0	<1.0	<1
Sodium	mg/kg dm	267	563	137	140	637
Strontium	mg/kg dm	396	444	378	380	467
Thallium	mg/kg dm	<1.0	<1	<1.0	<1.0	<1
Tin	mg/kg dm	2.11	1.67	2.0	2.14	1.24
Titanium	mg/kg dm	15.3	8.7	17.5	15.4	10.1
Vanadium	mg/kg dm	2.27	2.46	2.49	2.3	2.58
Zinc	mg/kg dm	122	41.2	120	118	44.6

[1]Single archived sample (analysed in February 2013); [2]Mean of 3 samples applied in October/November 2013; [3]Mean of 3 archived samples of the PS material applied at Harper Adams in September 2012 (analysed in February 2013).

3.3. Effect of fresh PS additions on topsoil chemical properties

Table 3.3 shows the effect of PS addition on topsoil chemical parameters, April 14.

Table 3.3 Effect of PS addition on topsoil chemical parameters, April 2014 (means)

Determinand	Unit	Gleadthorpe			Harper Adams		
		Control	Fresh PS	P statistic[2]	Control	Fresh PS	P statistic[2]
Nitrogen	% dm	0.10	0.08	*NS (0.54)*	0.16	0.13	*NS (0.11)*
Ammonium- N	mg/kg dm	<2	<2	*NS (1.0)*	<2	<2	*NS (1.0)*
Nitrate - N	mg/kg dm	<3	<3	*NS (1.0)*	5.34	5.19	*NS (0.86)*
Total carbon	% dm	1.27	1.40	*NS (0.48)*	1.59	1.63	*NS (0.85)*
C:N ratio	ratio	16.3	18.3	*NS (0.75)*	9.6	12.3	*NS (0.07)*
Conductivity	µs/cm	2120	2203	*NS (0.45)*	2123	2087	***0.008***
pH	unit	6.20	6.54	*NS (0.37)*	6.45	7.01	*NS (0.13)*
Extractable P	mg/l	43.3	51.1[1]	*NS (0.43)*	89.7	88.8	*NS (0.92)*
Extractable K	mg/l	62.8	75.8	*NS (0.30)*	119	148	***0.016***
Extractable mg	mg/l	62.3	42.8	***0.03***	48.0	47.5	*NS (0.89)*
Aluminium	mg/kg dm	4453	4940	*NS (0.17)*	11367	11133	*NS (0.66)*
Antimony	mg/kg dm	<1	1.02	*NS (1.0)*	1.08	<1	*NS (0.52)*
Arsenic	mg/kg dm	4.52	4.41	*NS (0.68)*	6.89	6.75	*NS (0.83)*
Barium	mg/kg dm	22.1	23.6	*NS (0.06)*	64.2	61.3	*NS (0.59)*
Beryllium	mg/kg dm	0.31	0.35	*NS (0.17)*	0.56	0.54	*NS (0.66)*
Boron	mg/kg dm	2.64	3.50	*NS (0.15)*	8.70	7.77	*NS (0.41)*
Cadmium	mg/kg dm	<0.2	<0.2	*NS (1.0)*	<0.2	<0.2	*NS (1.0)*
Calcium	mg/kg dm	1006	1852	*NS (0.22)*	2610	2483	*NS (0.78)*
Chromium	mg/kg dm	6.70	6.73	*NS (0.92)*	15.4	15.4	*NS (0.96)*
Chromium VI	mg/kg dm	<0.6	<1.2	*NS (1.0)*	<1.2	<0.6	*NS (1.0)*
Cobalt	mg/kg dm	1.84	1.78	*NS (0.45)*	4.57	4.11	***0.05***
Copper	mg/kg dm	4.27	5.34	***0.02***	13.2	13.4	*NS (0.73)*
Iron	mg/kg dm	7040	7117	*NS (0.76)*	12133	11767	*NS (0.74)*
Lead	mg/kg dm	15.8	15.0	*NS (0.60)*	19.9	18.2	*NS (0.19)*
Lithium	mg/kg dm	5.91	6.62	*NS (0.41)*	15.2	15.0	*NS (0.85)*
Magnesium	mg/kg dm	671	683	*NS (0.92)*	2443	2417	*NS (0.84)*
Manganese	mg/kg dm	185	148	*NS (0.14)*	312	284	*NS (0.47)*
Mercury	mg/kg dm	<0.2	<0.2	*NS (1.0)*	<0.2	<0.2	*NS (1.0)*
Molybdenum	mg/kg dm	<1	<1	*NS (1.0)*	<1	<1	*NS (1.0)*
Nickel	mg/kg dm	3.97	4.40	*NS (0.28)*	11.4	11.5	*NS (0.87)*
Phosphorus	mg/kg dm	514	601	*NS (0.24)*	1167	1147	*NS (0.86)*
Potassium	mg/kg dm	656	700	*NS (0.39)*	2263	2283	*NS (0.79)*
Selenium	mg/kg dm	<1	<1	*NS (1.0)*	<1	<1	*NS (1.0)*
Silver	mg/kg dm	<1	<1	*NS (1.0)*	<1	<1	*NS (1.0)*
Sodium	mg/kg dm	23.7	27.8	*NS (0.07)*	62.6	60.6	*NS (0.74)*
Strontium	mg/kg dm	4.25	5.89	*NS (0.07)*	9.80	9.13	*NS (0.54)*
Thallium	mg/kg dm	<1	<1	*NS (1.0)*	<1	<1	*NS (1.0)*
Tin	mg/kg dm	<1	1.04	*NS (1.0)*	1.32	<1	*NS (0.77)*
Titanium	mg/kg dm	77.6	75.6	*NS (0.59)*	119	116	*NS (0.61)*
Vanadium	mg/kg dm	10.0	9.94	*NS (0.62)*	19.2	18.4	*NS (0.58)*
Zinc	mg/kg dm	25.0	27.5	*NS (0.13)*	65.3	63.0	*NS (0.58)*
E-coli,confirmed	No/g	<1	<1	*NS (1.0)*	<1	<1	*NS (1.0)*

[1]Mean of 2 replicate plots; [2]Statistical analysis undertaken by t-test; NS = not significant (P>0.05); numbers in brackets indicate the P statistic.

There was a small (*c.*0.3-0.6 pH units) but not statistically significant (*P*>0.05) increase in topsoil pH *c.*6 months following the addition of fresh PS material relative to the untreated control. However, overall a single 30 t/ha application of PS had very little effect on topsoil chemical properties. Statistical analysis of the changes over time between the sampling undertaken in September 2013 (Table 3.1) prior to PS application and that undertaken in April 2014 *c.*6months after PS was applied (Table 3.3), is presented in Appendix 4. There was very little change (*P*>0.05) in most soil properties over this time period, with any significant changes (notably total C and conductivity, which increased over time; *P*<0.01), occurring on both treatments and, therefore, attributable to variations in sampling or analysis. Differences in topsoil extractable Mg concentrations measured at the outset of the experiment, prior to fresh PS additions, were still apparent at Gleadthorpe.

The differences in extractable K concentrations were also still apparent at Harper Adams and can be attributed to background soil variability. Here the apparently higher topsoil conductivity and cobalt concentrations on the untreated control treatment can also be attributed to background soil variability. However fresh PS additions did result in a small increase in topsoil copper concentrations at Gleadthorpe in April 2014 (Table 3.3, *P*<0.05) although total Cu concentrations were low, and well below toxicity thresholds (DoE, 1996). This effect was not repeated at Harper Adams.

Table 3.4 shows soil microbial biomass C and N and aggregate stability following a fresh application of paper sludge, Spring 2014. Fresh PS additions also had very little effect on topsoil microbial biomass and aggregate stability. Aggregate stability was similar to that measured at the baseline sampling (Table 3.1), whereas the microbial biomass decreased between September 2013 and April 2014 at Gleadthorpe (*P*<0.01; statistical results presented in Appendix 4; not observed at Harper). The microbial biomass is very dynamic in soil and will respond to weather, carbon input and season (Rice *et al.,* 1996). The changes observed at Gleadthorpe occurred on both the control and fresh PS treatments and are most likely due to seasonal variation in soil moisture and temperature.

Table 3.4 Soil microbial biomass C and N and aggregate stability

Treatment	Biomass C (mg/kg soil)		Biomass N (mg/kg soil)		Aggregate stability (% w/w)[3]	
Site[1]	GT	HA	GT	HA	GT	HA
Control	55 (6.1)	179 (19.4)	18 (2.8)	26 (0.6)	16 (0.6)	7 (1.2)
Fresh PS	39 (1.9)	153 (23.4)	14 (2.0)	30 (2.2)	16 (2.0)	7 (1.9)
P[2]	*NS (0.07)*	*NS (0.44)*	*NS (0.32)*	*NS (0.19)*	*NS (0.80)*	*NS (0.93)*

Standard errors in parenthesis; n=3..

[1]GT: Gleadthorpe; HA: Harper Adams; [2] Statistical analysis undertaken by t test; *NS*=not significant (*P*>0.05); numbers in brackets indicate the P statistic; [3]Aggregate stability measured by the dispersion ratio (ratio of silt and clay suspended by mild slaking forces expressed as a % of the total silt and clay content); Ratios in the range 6-10% suggest the soil is 'stable', 11-15% indicate that the soil is 'fairly stable', while ratios in the range 16-25% suggest the soil is 'somewhat unstable' (Anon, 1982).

3.4. Effect of historic repeated PS additions on topsoil chemical properties (January 2013)

The lack of any measurable differences in key soil properties following a single PS application at a comparatively low application rate is not surprising as it has been shown that repeated and relatively large organic material additions are needed to produce measurable changes in soil properties (Bhogal *et al.,* 2009; 2011). However, as PS is likely to be applied on more than one occasion within an agricultural rotation, the longer-term effects of such applications are particularly important. Previous sampling of the historic PS treatment plots at Gleadthorpe and Harper Adams experimental sites undertaken as part of the SOIL-*QC* experimental programme in 2006/07 (Defra, 2011) concluded that even after 2-3 years of repeated PS additions changes in soil properties (particularly soil physical properties) were small and difficult to detect.

The chemical analysis of the topsoil (0-15cm) undertaken in January 2013 on the historic PS plots which had received 6-9 annual PS additions (Table 2.1) therefore provided a valuable opportunity to evaluate the longer-term effects of repeated PS additions, which is often lacking from many studies (Gibbs *et al.,* 2005). The analyses performed in January 2013 were undertaken at a different laboratory to those in 2006/07 and only topsoil carbon, nitrogen, pH and microbial biomass were common to both sampling times. Despite this, the results were used to evaluate the effect of 2-3 years of PS addition (sampled in 2006 at Gleadthorpe and 2007 at Harper Adams) compared with 6-9 years of addition (sampled in 2013 at both sites).

Topsoil pH was elevated at both sites and on both sampling occasions following repeated additions of PS for either 2-3 or 6-9 years (*P*<0.001; **Error! Reference source not found.**), confirming the value of PS as a liming material, with the pH on the control plots remaining fairly constant (at *c.* pH 6.0) over the 7 year period. After 2-3 years of PS addition, at rates ranging between 30 and 75 t/ha (fresh weight), the topsoil pH had increased by 0.5-1.0 units, whereas after 6-9 years of repeated addition this difference had increased to *c*.2 pH units.

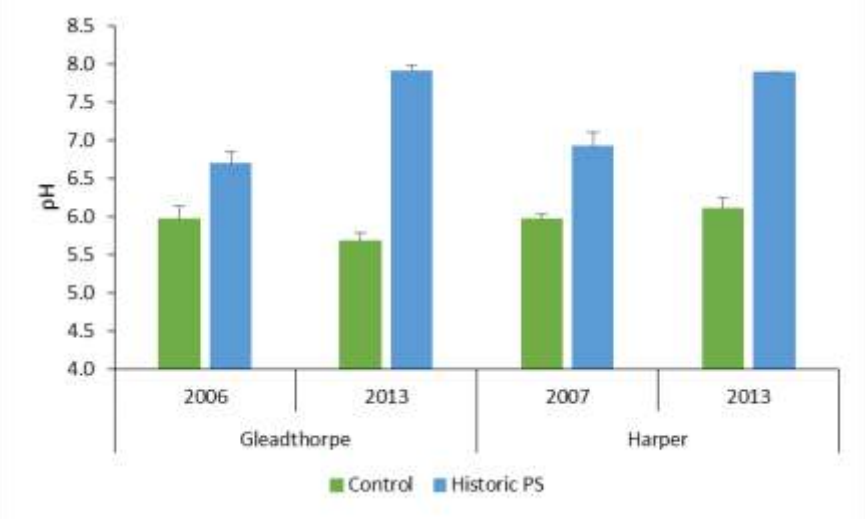


Figure 3.1 Effect of repeated historic PS additions on topsoil pH
Statistical analysis: both sites *P*<0.001 for treatment, with no change on the control plots, but a significant increase on the PS treated plots over time.

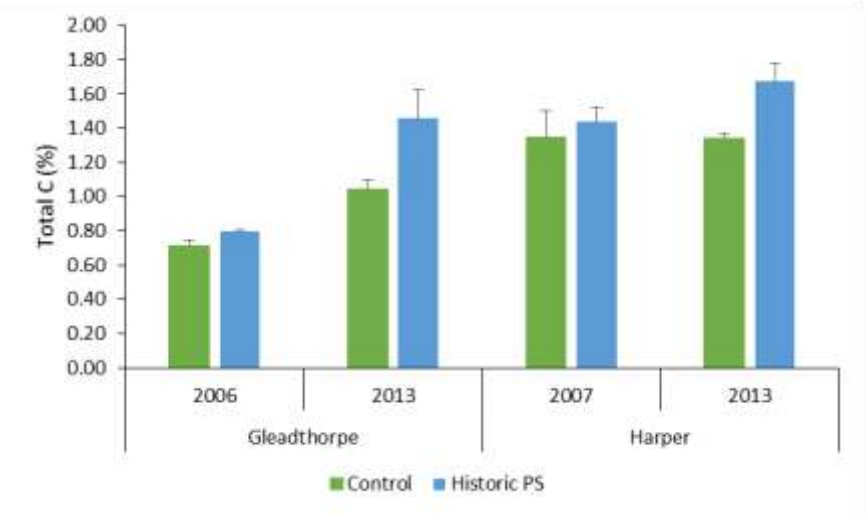


Figure 3.2 Effect of repeated historic PS additions on topsoil carbon content
Statistical analysis: *P*<0.05 for treatment at Gleadthorpe, with a significant increase in C over time; *P*<0.05 for treatment at Harper in 2013 only (no changes over time)

A total of 10-12 t/ha C was applied with the PS during the first 2-3 years of experimentation, resulting in a small increase in topsoil C at both sites (Figure 3.2). Over the following 5-6 years a further 15-20 t/ha C was applied with the repeated PS additions, resulting in further increases in topsoil C (P<0.05; Figure 3.3) which equated to *c.*6-8 t/ha additional C in the topsoil. Such increases in topsoil C are likely to lead to improvements in soil quality and fertility (e.g. Johnston *et al*., 2009). Indeed, topsoil microbial biomass C and N, an indicator of soil biological health, increased at Harper Adams in 2006 and at both sites in 2013 (P<0.05; Figure 3.3 and Figure 3.4).

There was very little effect of the repeated PS additions on the additional soil properties measured in 2013 (P>0.05; full data set in Appendix 5). Only topsoil strontium concentrations increased from *c.*3mg/kg on the untreated control to 16 mg/kg on the historic PS treatment at Gleadthorpe and from *c.*8 mg/kg on the untreated control to 28 mg/kg on the historic PS treatment at Harper Adams (P<0.05), although these concentrations are still low and well within the range of reported values for typical agricultural soils (Rawlins *et al*., 2012).

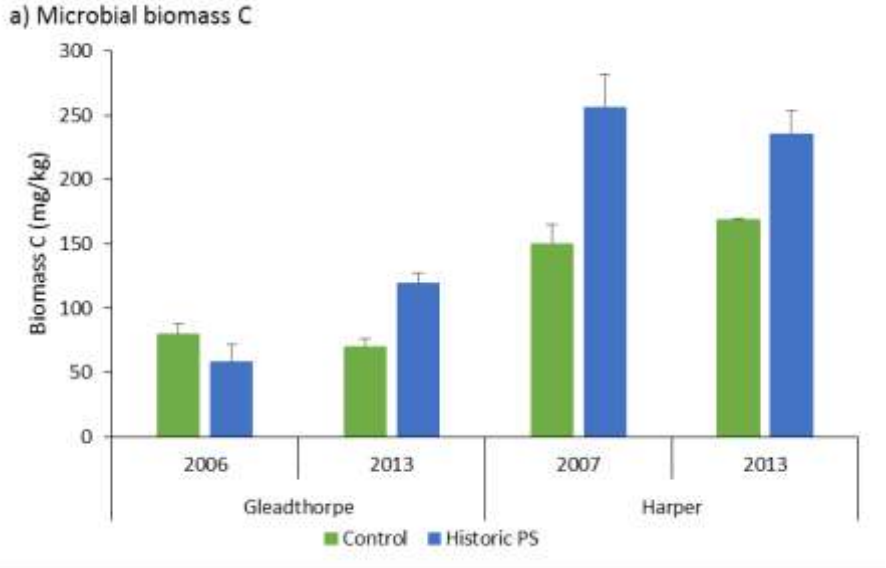


Figure 3.3 Effect of repeated historic PS additions on topsoil microbial biomass C
Statistical analysis: P<0.05 for treatment in 2013 only at Gleadthorpe; P<0.01 for treatment at Harper (both years), with no changes over time.

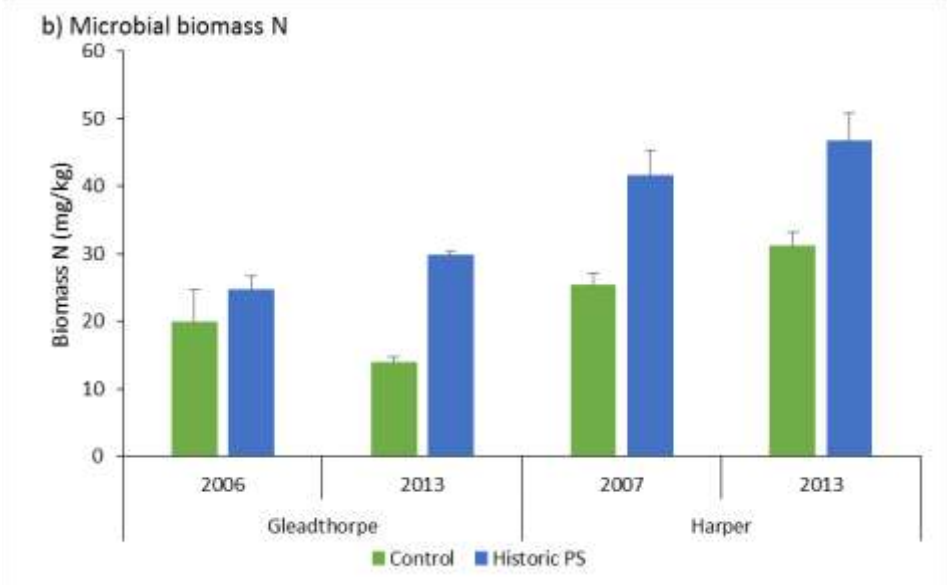


Figure 3.4 Effect of repeated historic PS additions on topsoil microbial biomass N
Statistical analysis: P<0.05 for treatment at Gleadthorpe in 2013 only (no changes over time); P<0.001 for treatment at Harper (both years), with no changes over time.

3.5. Effect of fresh PS additions on grain yield and uptake of potential chemicals of concern

The single application of fresh PS had no effect (*P*>0.05) on grain yields at harvest 2014 at either site, although winter wheat yields were *c*.1.4 t/ha higher on the fresh PS treatment at Gleadthorpe and spring barley yields were *c*.0.2 t/ha higher on the fresh PS treatment at Harper Adams (Table 3.5). This is likely to reflect the additional 40 kg/ha manufactured fertiliser N that was applied to the fresh PS treatment to account for potential N immobilisation following the PS additions.

Table 3.5 Effect of fresh PS additions on winter wheat grain yield, nutrient and metal concentrations, harvest 2014

Determinand	Unit	Gleadthorpe (winter wheat)			Harper Adams (spring barley)		
		Control	Fresh PS	P statistic[1]	Control	Fresh PS	P statistic[1]
Grain yield	t/ha @ 85% dm	5.40	6.76	NS (0.09)	3.05	3.25	NS (0.43)
Aluminium	mg/kg dm	<50	<50	NS (1.0)	59.5	<50	NS (1.0)
Antimony	mg/kg dm	<1	<1	NS (1.0)	<1	<1	NS (1.0)
Arsenic	mg/kg dm	1.08	1.09	NS (0.63)	1.14	1.14	NS (0.96)
Barium	mg/kg dm	4.41	4.38	NS (0.93)	2.32	2.37	ND (0.45)
Beryllium	mg/kg dm	<0.1	<0.1	NS (1.0)	<0.1	<0.1	NS (1.0)
Boron	mg/kg dm	2.77	2.38	NS (0.56)	3.09	2.69	NS (0.45)
Cadmium	mg/kg dm	<0.2	<0.2	NS (1.0)	<0.2	<0.2	NS (1.0)
Calcium	mg/kg dm	440	542	NS (0.31)	712	583	NS (0.36)
Chromium	mg/kg dm	<0.5	<0.5	NS (1.0)	<0.5	0.55	NS (1.0)
Cobalt	mg/kg dm	<0.1	<0.1	NS (1.0)	<0.1	<0.1	NS (1.0)
Copper	mg/kg dm	2.37	2.10	**0.04**	2.17	2.37	NS (0.18)
Iron	mg/kg dm	<200	<200	NS (1.0)	<200	<200	NS (1.0)
Lead	mg/kg dm	<1	<1	NS (1.0)	<1	<1	NS (1.0)
Lithium	mg/kg dm	<1	<1	NS (1.0)	<1	<1	NS (1.0)
Magnesium	mg/kg dm	995	966	NS (0.70)	876	943	NS (0.29)
Manganese	mg/kg dm	29.1	26.6	NS (0.42)	12.4	11.7	NS (0.75)
Mercury	mg/kg dm	<1	<1	NS (1.0)	<1	<1	NS (1.0)
Molybdenum	mg/kg dm	<1	<1	NS (1.0)	<1	<1	NS (1.0)
Nickel	mg/kg dm	<0.6	<0.6	NS (1.0)	<0.6	<0.6	NS (1.0)
Phosphorus	mg/kg dm	3433	3200	NS (0.45)	3553	4063	**0.018**
Potassium	mg/kg dm	4957	4730	NS (0.11)	5533	5200	NS (0.39)
Selenium	mg/kg dm	1.08	1.12	NS (0.19)	1.26	1.29	NS (0.69)
Silver	mg/kg dm	<1	<1	NS (1.0)	<1	<1	NS (1.0)
Sodium	mg/kg dm	13.4	26.1	NS (0.21)	53.2	36.7	NS (0.30)
Strontium	mg/kg dm	1.89	2.6	NS (0.16)	1.52	1.11	NS (0.27)
Thallium	mg/kg dm	<1	<1	NS (1.0)	<1	<1	NS (1.0)
Tin	mg/kg dm	<1	<1	NS (1.0)	<1	<1	NS (1.0)
Titanium	mg/kg dm	<3	<3	NS (1.0)	<3	<3	NS (1.0)
Vanadium	mg/kg dm	<0.1	<0.1	NS (1.0)	0.12	<0.1	NS (1.0)
Zinc	mg/kg dm	33.0	29.6	NS (0.42)	24.3	31.4	**0.005**

[1]Statistical analysis undertaken by t test; NS=not significant (*P*>0.05); numbers in brackets indicate the P statistic.

There was also no effect of the fresh PS additions on the uptake of PCOCs into the grain (Table 8). Only total Zn concentrations in the grain were marginally increased on the fresh PS treatment at Harper Adams (*P*<0.01; Table 3.5). But as Zn concentrations in the applied material were low (Table 3.2) and there were no differences in topsoil Zn concentrations (Table 3.3). This may be the result of random site variability, particularly as there was no statistical difference at Gleadthorpe, with the grain from the control treatment having a numerically higher zinc concentration.

It was observed towards the end of the study that the alkalinity of the storage heap increased sharply. The reasons for this pH increase are unclear as the bulk chemistry of the heap remained relatively unchanged. The final alkalinity of the heap (pH 9.7 – 9.8), while much higher than the original material pH, is broadly consistent with the range of values reported for other commonly used liming materials.

3.6. Storage study

Over the course of the storage period the total weight of PS material within each of the storage heaps decreased by *c*.25%, equivalent to a loss of *c*.1.25 tonnes (**Error! Reference source not found.**). This was most likely due to decomposition (oxidation) of the organic fraction of the PS material, with both the total C and organic matter content decreasing during the course of the *c.*12 month storage period (*P*<0.01; Figure 3.6 & Table 3.5). The temperature of the heaps was also elevated above ambient air temperatures for the first 3-4 months of storage, suggesting the material was still biologically active and decomposing (Figure 3.7). However the N content, although variable, did not decline over time (*P*<0.05 by ANOVA but *P*>0.05 by regression; Table 3.6) resulting in a decrease in the C:N ratio (from 66:1 to 50:1; *P*<0.01, r^2=48%).

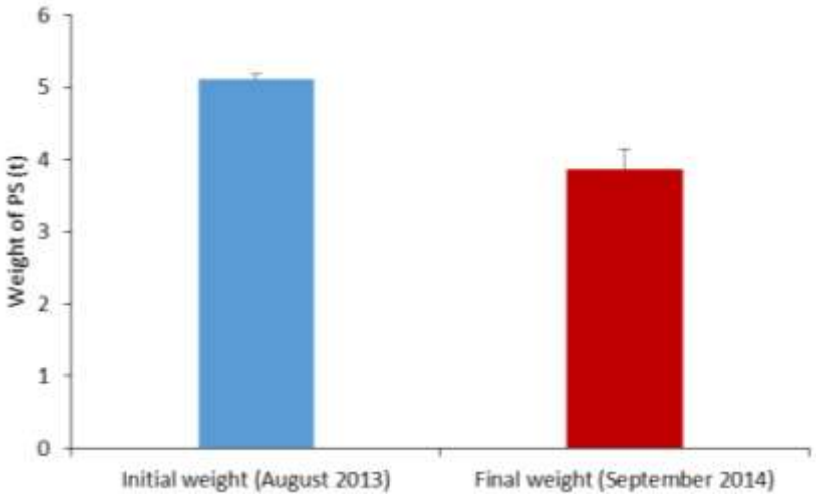


Figure 3.5 Change in weight of PS with storage

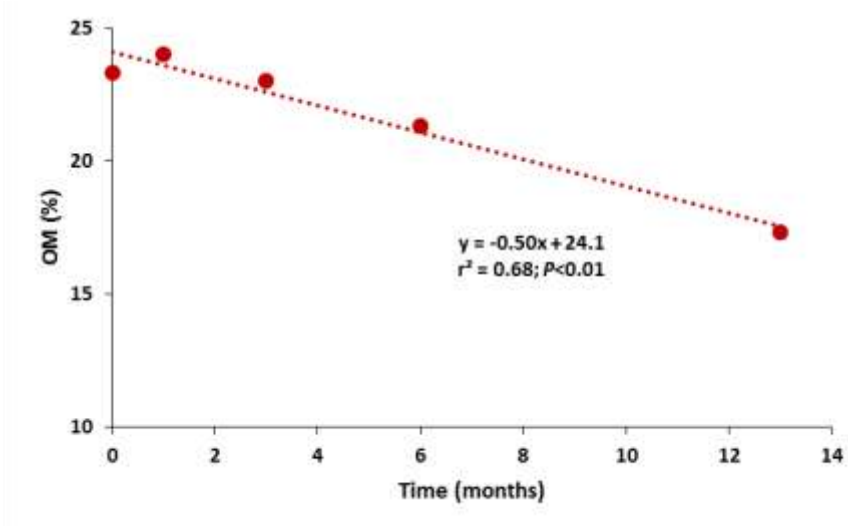


Figure 3.6. Decline in organic matter content of the PS material during storage

Although there was some variability in the concentration of other nutrients and metals throughout the storage period (Table 3.5) the only consistent variation was for total sulphur, which decreased to negligible concentrations over the c.12 month period, and total manganese and strontium, whose concentrations increased by 10-15% ($P<0.05$; Table 3.5). It is surprising that the concentration of other immobile metals did not increase over time given the loss of organic matter. This is most likely a consequence of variability in analysis and low concentrations of many of these elements at the outset. E.coli was present at the start of the storage period, possibly due to the presence of some biologically treated material within the batch of PS (Table 3.6), but after just 1 month of storage these had died off, in line with similar work undertaken with farm manures (Nicholson et al., 2005).

These results suggest that apart from oxidation of the organic matter leading to a reduction in the total volume of material stored, there was very little change in the composition the PS with storage. However, weeds readily established on the heaps from early spring onwards, such that by the end of the storage period there was a considerable weed biomass which had to be destroyed prior to dismantling the heaps (Figure 3.8).

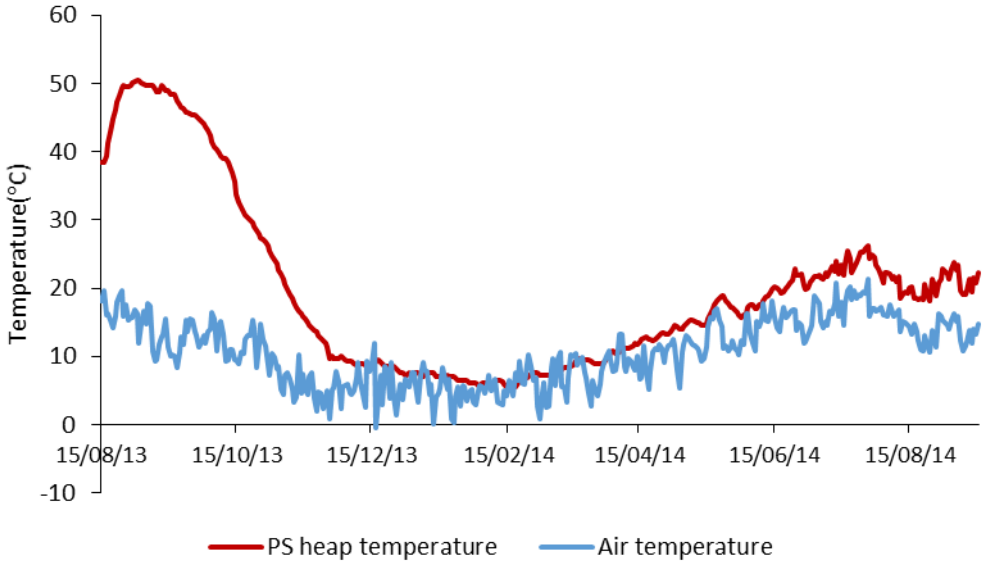


Figure 3.7 Average daily air and heap temperatures

Figure 3.8 Paper sludge heaps at the start (a) and end (b) of the storage period

Table 3.6 Changes in PS composition with storage (mean of 3 replicate heaps)

Determinand	Unit	Aug. 2013	Sept. 2013	Nov. 2013	Feb. 2014	Sept. 2014	ANOVA[1]	Regression[2]		
							P	P	r^2	↕
Dry matter	%	71.1	80.6	63.9	64.9	75.3	**0.003**	NS		
pH	unit	7.4	8.1	7.7	9.8	9.7	**0.008**	**0.003**	**46%**	↑
Total neutralising	% fw	26.5	45.0	23.8	23.9	31.9	**0.008**	NS		
Conductivity	µS/cm	1069	706	717	nd	2283	**<0.001**	**<0.001**	**76%**	↑
LOI	% dm	24.7	22.3	19.9	19.1	18.9	**<0.001**	**<0.001**	**53%**	↓
Organic matter	% dm	23.3	24.0	23.0	21.3	17.3	**0.007**	**<0.001**	**68%**	↓
Total carbon	% dm	21.2	19.9	19.0	18.3	18.4	**<0.001**	**<0.002**	**48%**	↓
C:N ratio	ratio	66.5	61.7	54.0	58.7	50.5	**0.004**	**0.003**	**48%**	↓
Total nitrogen	kg/t fw	2.27	2.62	2.25	2.03	2.76	**0.03**	NS		
Phosphate (P_2O_5)	kg/t fw	0.96	0.75	0.62	0.78	0.95	NS (0.69)	NS		
Potash (K_2O)	kg/t fw	0.89	0.45	0.45	0.79	0.83	NS (0.61)	NS		
Magnesium (MgO)	kg/t fw	3.36	3.72	3.10	3.19	3.73	NS (0.21)	NS		
Sulphur (SO_3)	kg/t fw	0.53	0.02	<0.02	<0.02	0.0	**<0.001**	**0.05**	**21%**	↓
Calcium	kg/t fw	165	195	163	165	200	**0.02**	NS		
Aluminium	mg/kg dm	6150	5360	5637	6037	5257	**0.04**	NS		
Antimony	mg/kg dm	<1	<1	<1	<1	<1	N/A			
Arsenic	mg/kg dm	1.0	0.9	0.9	1.0	0.85	NS (0.18)	NS		
Barium	mg/kg dm	73.4	76.0	67.3	76.3	77.4	NS (0.06)	NS		
Beryllium	mg/kg dm	<0.1	<0.1	<2	0.1	<0.1		NS		
Boron	mg/kg dm	3.6	<1	2.0	2.5	3.3	NS (0.26)	NS		
Cadmium	mg/kg dm	<0.2	<0.2	<0.2	<0.2	<0.2	N/A			
Chromium	mg/kg dm	12.6	12.5	12.9	13.2	12.1	NS (0.18)	NS		
Chromium VI	mg/kg dm	<0.3	<0.6	<0.6	<0.6	<0.6	N/A			
Cobalt	mg/kg dm	1.2	1.1	1.3	1.3	1.2	**0.006**	NS		
Copper	mg/kg dm	161	166	158	171	158	**0.03**	NS		
Iron	mg/kg dm	898	803	759	<4000	837	NS (0.12)	NS		
Lead	mg/kg dm	8.8	12.7	8.3	9.3	8.3	NS (0.21)	NS		
Lithium	mg/kg dm	6.2	11.6	12.5	15.6	9.6	**<0.001**	NS		
Manganese	mg/kg dm	103	98.3	88.9	118	120	**0.004**	**0.01**	**36%**	↑
Mercury	mg/kg dm	<0.2	<0.2	<0.2	<0.2	<0.2	N/A			
Molybdenum	mg/kg dm	1.1	<1	1.0	1.0	<1	N/A			
Nickel	mg/kg dm	4.1	3.9	4.2	4.3	4.2	NS (0.11)	NS		
Selenium	mg/kg dm	<1	<1	<1	<1	<1	N/A			
Silver	mg/kg dm	<1	<1	<1	<1	<1	N/A			
Sodium	mg/kg dm	658	561	731	472	576	NS (0.35)	NS		
Strontium	mg/kg dm	440	449	431	490	471	**0.001**	**0.03**	**26%**	↑
Thallium	mg/kg dm	<1	<1	<1	<1	<1	N/A			
Tin	mg/kg dm	1.2	1.1	1.2	1.2	1.3	NS (0.19)	NS		
Titanium	mg/kg dm	7.3	9.0	9.6	8.7	9.4	NS (0.35)	NS		
Vanadium	mg/kg dm	2.6	2.4	2.5	2.6	2.3	NS (0.06)	NS		
Zinc	mg/kg dm	49.2	45.5	41.1	47.4	48.5	NS (0.82)	NS		
E. Coli (confirmed)	No/g fw	31800	<1	<10	12.3	1.0	NS (0.20)	NS		
Salmonella	Pres/abs	0.0	0.0	0.0	0.0	0.0	N/A			

[1]Statistical analysis undertaken using ANOVA (data normally distributed); NS=not significant (*P*>0.05); N/A=not applicable (results below the limit of detection); numbers in brackets indicate the P statistic; [2]Statistical analysis undertaken using Regression; NS=not significant (P>0.05), r^2 = percentage of variance accounted for; ↕=direction of change (↑= increase; ↓decrease)

A total of 577mm of water drained from the PS heaps over the storage period equating to *c.*75% of the total rainfall (745mm) that fell over the same period (

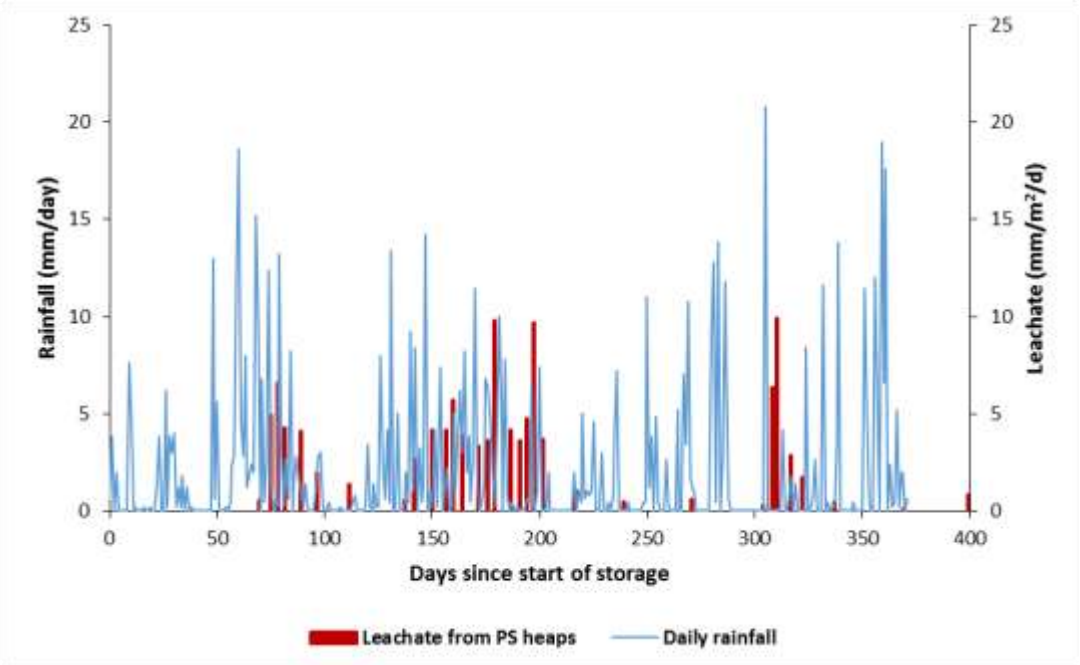


Figure 3.9). Total N concentrations in the leachate decreased over the storage period (*P*<0.001; Figure 3.10 & Table 3.6) and amounted to a total of 0.38kg (equivalent to *c.*3% of the total N stored in the PS heap; Table 3.8). Nitrate concentrations peaked over the winter months (December – March) reflecting the higher rainfall, and exceeded the Nitrate Directive limit of 11.3 mg/l nitrate-nitrogen (or 50 mg/l nitrate) for the duration of this period (EU, 2006a). Ammonium-N concentrations exceeded the Freshwater Fish Directive limit value of 0.78 mg/l (EU, 2006a) at the outset of the storage period but by January 2014 concentrations had fallen to acceptable levels (*P*<0.001; r^2=29%; Figure 3.10 & Table 3.6).

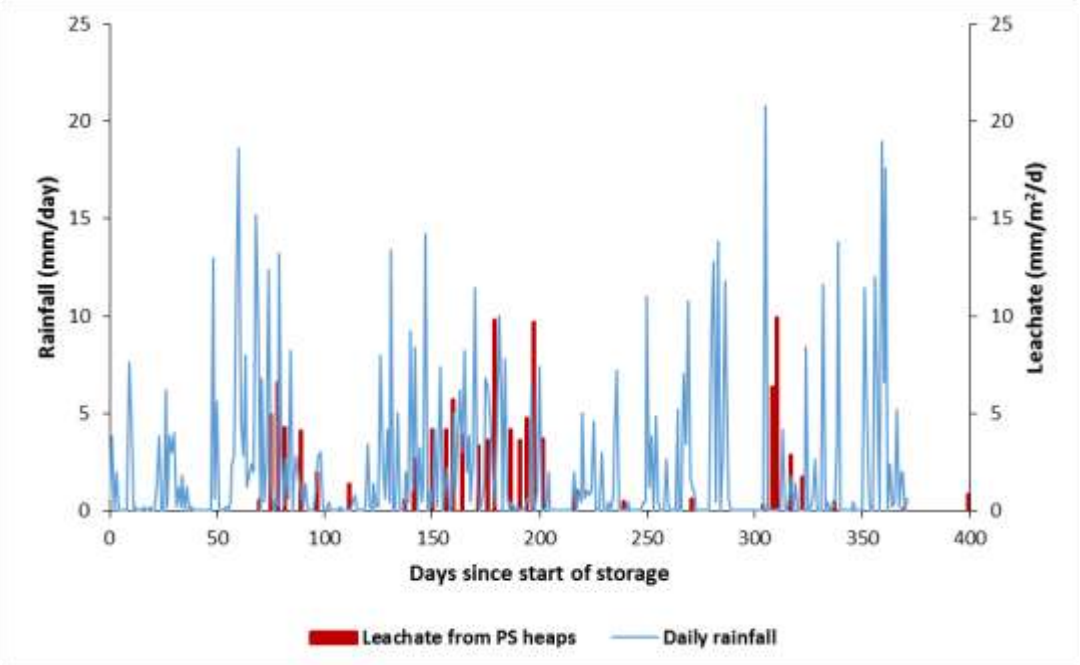


Figure 3.9 Leachate loss patterns and total rainfall during storage of the PS materials

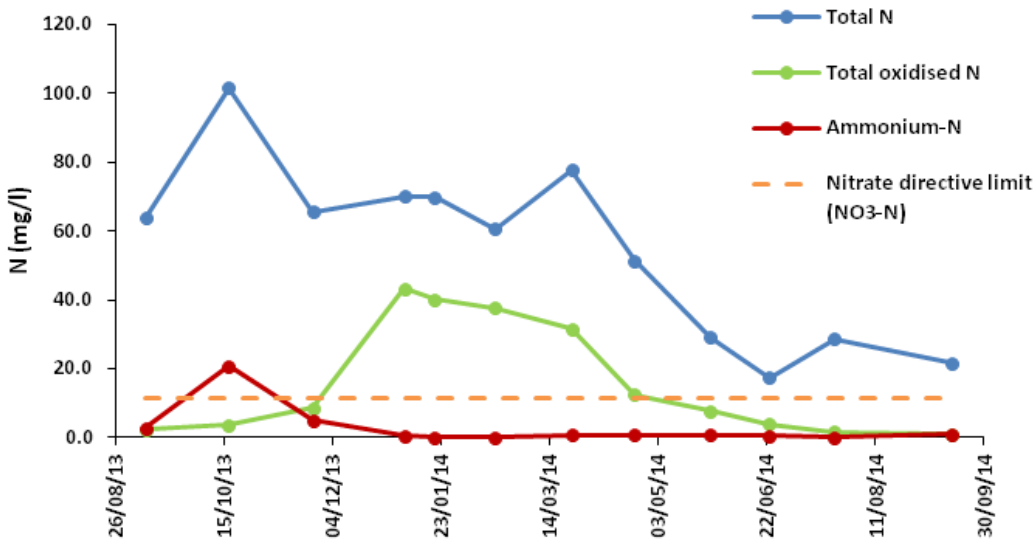


Figure 3.10 Nitrogen concentrations in water draining from the PS storage heaps

Standards for the concentrations of molybdate reactive P (MRP) in rivers were recently updated as part of the UK's implementation of the Water Framework Directive (Anon, 2014). Here, lowland rivers with a MRP concentration of <0.11 mg/l are considered to be of moderate or good quality whilst concentrations >0.8mg/l are considered to be poor quality (Anon, 2014). Concentrations of orthophosphate P in the leachate from the PS heaps exceeded this level for the majority of the storage period (Figure 3.11) although overall total P losses were less than 1% of the P stored in the PS heaps (Table 3.8).

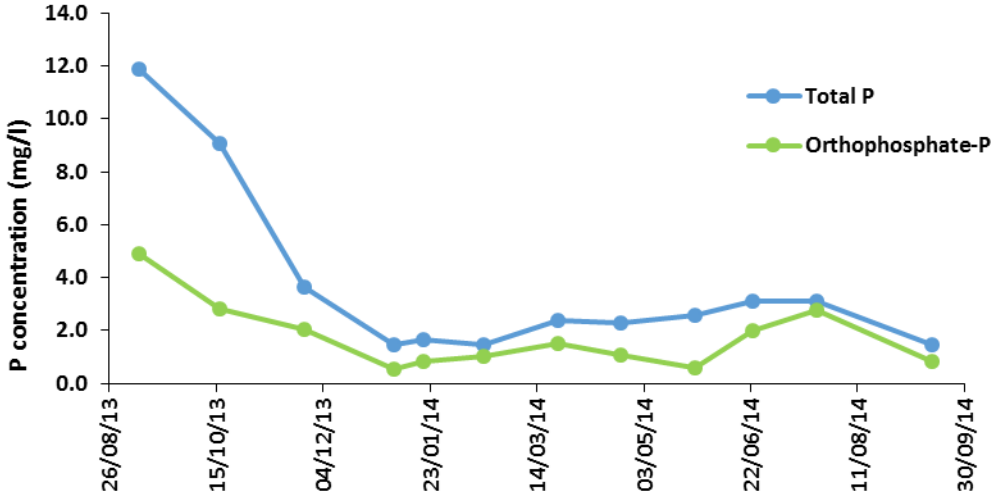


Figure 3.11 Phosphorus concentrations in water draining from the PS storage heaps

BOD of the leachate was elevated at the outset of the storage period (Figure 3.12) but dropped to low levels within 1 month (P<0.001; r^2=27%; Table 3.6). To contextualise these; pig slurry typically has a BOD level of 20,000-30,000 mg/l, cattle slurry 10,000-20,000 mg/l and dirty water 1,000-5,000 mg/l (MAFF, 1998), whilst treated sewage sludge effluent must typically meet a BOD discharge consent of <20mg/l before entering a surface water system. The BOD of leachate from

the PS heaps at <1000mg/l was considerably lower than the BOD of farm manures and after c.1 month storage had dropped to <20mg/l in the majority of samples. The laboratory reporting limit was elevated to 30mg/l for three samples (due to eg sample interference) so it can not be confirmed whether these samples were also <20mg/l.. E-coli was also only present in the leachate up to 2 months following storage, reflecting the die-back of this indicator organism within the PS material itself (Figure 3.13). However, numbers did exceed the Bathing Water Directive (2006/7EC) threshold of 500/100ml during this period (EU, 2006b).

There was considerable variation in the concentrations of other nutrients and metals within the leachate (P<0.05; by ANOVA). The concentration is a function of both the quantity leached and volume of leachate. As can be seen from Table 3.7, the volume collected in the drainage tanks varied over the year, reflecting rainfall patterns (Figure 3.9), with most rainfall over the winter months, and only small volumes collected in July. This could lead to more diluted leachate over winter and increasing concentrations in the summer. However, for the majority of parameters, the tendency was for a decline in concentration over time (Table 3.7). For most parameters the total amount leached represented only a very small proportion of that stored in the heaps (<5%; Table 3.8). Where there were significant changes in heap composition (i.e. total N, Al, Co, Cu and Mn), leaching losses accounted for up to 40% of these changes (Table 3.8). It is likely that changes in heap composition, which could not be accounted for by leaching, are due to variability in sampling and analysis.

Table 3.7 Composition of leachate draining from the PS heaps

(mean of 3 replicate heap, except in September when only 1 heap was draining)

Determinand	Sample date												ANOVA[1]	Regression[2]		
	09/9/13	17/10/13	25/11/13	06/1/14	20/1/14	17/2/14	24/3/14	22/4/14	27/5/14	23/6/14	23/7/14	15/9/14	P	P	r^2	↕
Volume of water in tank on sample date (l)	55	203	190	297	238	150	100	163	260	69	26	235				
Total drainage between sampling dates (l)		203	1206	829	573	1485	249	163	349	535	26	235				
pH	7.4	7.7	8.4	8.0	8.2	8.2	8.4	8.3	8.0	8.1	7.9	7.6	**<0.001**	NS		
BOD (mg/l)	913	102	<29.2	10.9	11.6	7.63	<29.2	12.3	<29.2	8.0	13.9	4.3	**<0.001**	**0.001**	**27%**	↓
Total P (mg/l)	11.9	9.08	3.64	1.44	1.66	1.45	2.4	2.3	2.6	3.1	3.1	1.5	**<0.001**	**0.015**	**17%**	↓
Orthophosphate-P (mg/l)	4.91	2.81	2.04	0.54	0.85	1.01	1.5	1.1	0.6	2.0	2.8	0.8	NS (0.06)	NS		
Total N (mg/l)	63.8	102	65.7	70.0	69.9	60.6	77.8	51.5	29.0	17.3	28.7	21.7	**<0.001**	**<0.001**	**70%**	↓
Ammonium N (mg/l)	2.84	20.8	5.01	0.56	<0.5	<0.5	0.7	0.8	0.7	0.5	<0.5	1.0	**<0.001**	**<0.001**	**29%**	↓
Total oxidised N (mg/l)	2.40	3.60	8.53	43.3	40.1	37.6	31.5	12.3	7.8	3.8	1.6	1.0	**<0.001**	**0.02**	**14%**	↓
Aluminium (ug/l)	592	215	294	205	754	88.8	136	330	118	353	219	63.4	**<0.001**	NS		
Aluminium – Active (ug/l)	22.2	25.9	7.50	<4	nd	12.2	12.0	8.2	<4	10.5	8.0	7.5	**<0.001**	**0.003**	**31%**	↓
Antimony (ug/l)	2.03	<5	2.17	2.25	1.50	2.07	2.7	<1	<1	2.2	3.0	2.1	NS (0.73)	NS		
Arsenic (ug/l)	28.8	52.1	24.0	23.7	22.9	18.5	28.2	14.4	6.4	6.1	9.5	7.7	**<0.001**	**<0.001**	**61%**	↓
Barium (ug/l)	654	254	186	134	122	108	158	136	124	139	205	164	**0.04**	NS		
Beryllium (ug/l)	0.16	<2	<2	<1	<10	<1	<1	<2	<2	<2	<1	<1	N/A			
Cadmium (ug/l)	<0.6	<0.6	<0.6	<0.1	<0.5	0.22	0.1	0.1	0.1	0.4	1.1	0.6	N/A			
Chromium (ug/l)	3.12	7.42	5.77	3.77	5.24	3.18	11.8	6.0	1.8	<10	2.7	5.7	**<0.001**	NS		
Chromium HVI(ug/l)	<3.00	24.7	3.00	<3	<3	<3	<3.0	<3.0	<3.0	0.3	0.8	0.4	N/A			
Cobalt (ug/l)	15.8	49.6	28.3	24.2	22.4	15.9	27.5	22.7	10.8	8.9	10.1	9.9	**<0.001**	**<0.001**	**66%**	↓
Copper (ug/l)	21.9	110	72.3	119	108	84.5	102	50.0	30.7	28.5	68.7	56.9	**<0.001**	**<0.001**	**37%**	↓
Lead (ug/l)	6.03	<5	<5	<2	6.10	<2	<2.0	<2.0	<2.0	2.3	13.0	2.0	N/A			
Manganese (ug/l)	377	140	64.5	41.3	40.2	32.3	43.5	49.4	46.3	62.7	101	55.6	**<0.001**	NS		
Mercury (ug/l)	0.04	<0.2	<0.2	0.05	0.03	<0.1	0.1	0.3	0.1	0.0	0.1	0.1	N/A			
Molybdenum (ug/l)	4.70	38.9	45.1	68.2	182	49.1	70.4	22.2	22.0	<20	16.5	68.9	**<0.001**	NS		
Nickel (ug/l)	27.2	116	94.9	70.1	66.4	52.0	98.6	78.7	29.7	37.9	21.8	22.7	**<0.001**	**<0.001**	**63%**	↓
Selenium (ug/l)	<1	2.17	2.21	<1	1.02	<1	1.0	<1	<1	<1	<1	<1	N/A			
Silver (ug/l)	<0.7	0.91	<0.7	<0.7	<17.5	<0.7	<0.4	<3.5	<3.5	<7	0.8	<0.7	N/A			
Tellurium (ug/l)	<0.4	<0.4	<0.2	<0.2	<2	<0.2	<0.2	<0.2	<0.4	<0.8	<0.2	<0.2	N/A			
Thallium (ug/l)	0.57	<0.5	1.87	<1	<20	<1	<1	<4	<4	<8	<1	<1	N/A			
Tin (ug/l)	<2.00	<5	<5	<2	<20	<2	<2	<4	<4	<8	<2	<2	N/A			
Titanium (ug/l)	7.32	11.0	11.4	6.9	<20	7.03	10.1	9.4	<4	8.2	16.7	5.4	**0.003**	NS		
Uranium (ug/l)	1.22	8.42	6.54	10.6	8.82	7.15	12.1	4.8	4.0	4.5	1.9	4.2	**<0.001**	**<0.001**	**30%**	↓

Determinand		Sample date											ANOVA[1]	Regression[2]		
	09/9/13	17/10/13	25/11/13	06/1/14	20/1/14	17/2/14	24/3/14	22/4/14	27/5/14	23/6/14	23/7/14	15/9/14	P	P	r^2	↕
Vanadium (ug/l)	<4.00	21.6	19.5	12.7	14.2	11.0	14.9	12.7	5.6	13.5	14.4	8.7	**<0.001**	**<0.001**	**30%**	↓
Zinc (ug/l)	86.3	92.2	53.3	38.6	<200	21.4	55.3	42.0	51.2	97.4	126	17.5	**0.002**	NS		
E-coli (No/100ml)	260,000	4233	145	75.0	75.0	49.5	30.0	15.7	45.3	<10	360	375	**<0.001**	**0.02**	**14%**	↓

[1]Statistical analysis undertaken using ANOVA (data normally distributed); NS=not significant (*P*>0.05); N/A=not applicable (results below the limit of detection); The first sampling date (September 2013) was excluded from the analysis as only one replicate heap was draining; numbers in brackets indicate the P statistic.

[2]Statistical analysis undertaken using Regression; NS=not significant (*P*>0.05), r^2 = percentage of variance accounted for; ↕=direction of change (↑= increase; ↓decrease). The first sampling date (September 2013) was excluded from the analysis as only one replicate heap was draining

Table 3.8 Total losses in relation to heap composition (mass balance)

Determinand	Total in heap (kg)		Change in heap		Total leached		
	Aug.13	Sept. 14	g[1]	% of initial heap content	g	% of initial heap content	% of change in heap
Total N	11.60	10.68	**926**	7.98	379	3.26	40.9
Total P	2.15	1.62	530	24.6	19.3	0.90	3.65
Aluminium	22.35	15.29	**7059**	31.6	1.80	0.01	0.03
Arsenic	0.004	0.002	1.11	31.1	0.14	3.92	15.0
Barium	0.267	0.225	41.6	15.60	0.95	0.36	3.70
Chromium	0.046	0.035	10.59	23.1	0.03	0.08	0.43
Cobalt	0.004	0.004	0.66	15.44	0.14	3.37	35.7
Copper	0.586	0.459	**128**	21.8	0.50	0.09	0.53
Manganese	0.376	0.349	**26.9**	7.14	0.38	0.10	17.8
Molybdenum	0.004	0.000	3.83	100	0.40	105	10.5
Nickel	0.015	0.012	2.54	17.3	0.42	2.88	25.3
Titanium	0.027	0.027	-0.75	-2.8	0.05	0.20	-1.96
Vanadium	0.009	0.007	2.68	28.4	0.09	0.91	3.91
Zinc	0.179	0.141	37.8	21.1	0.37	0.21	1.34

[1]Changes in bold are significant at $P<0.05$ by ANOVA (see Table 3.6); mass balance only calculated for those elements where concentrations in the leachate were greater than the analytical limits of detection.

These results show that leachate from PS heaps can contain elevated concentrations of multiple pollutants (e.g. nitrate-N, ammonium-N, phosphorus-P, BOD and *E-coli*), which could cause detrimental effects if they reached surface water bodies in an undiluted form. In practice pollutants in leachates infiltrating soil underneath a field heap of PS, or in runoff from the heap, are likely to be either retained in the soil or will mix with runoff from the rest of the field. Additionally, it should be noted that pollutant losses from the PS field heaps were well below (i.e. less than a tenth) leachate losses from solid manure heaps, in particularly for nitrogen/nitrate, phosphorus, BOD and *E-coli* (Nicholson *et al.*, 2013).

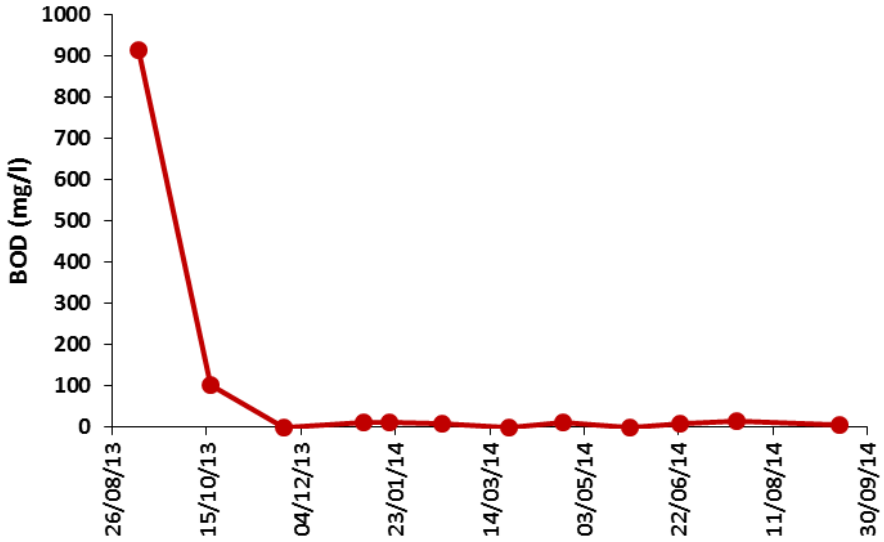
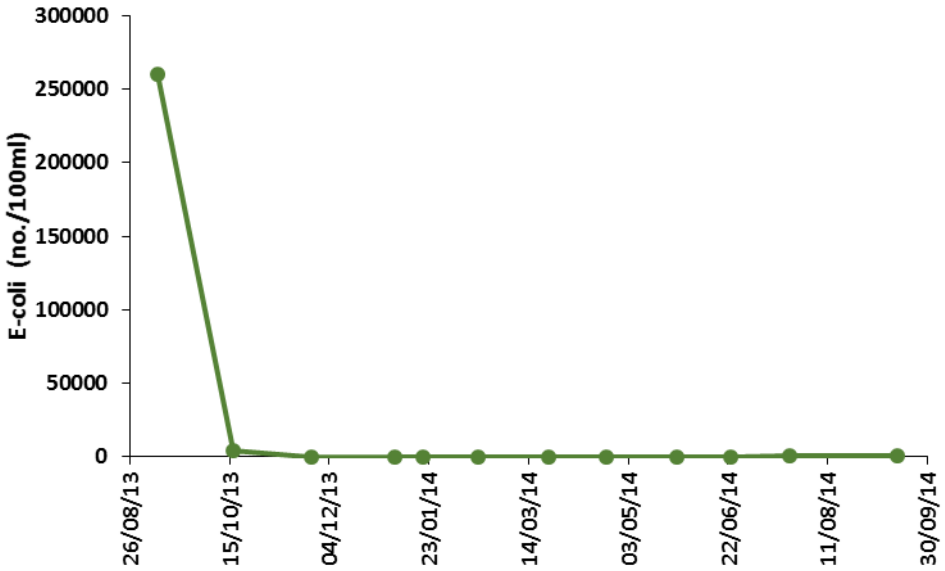


Figure 3.12 BOD of water draining from the PS storage heaps

In normal commercial operation the vast majority of paper mills would not be expected to store PS on site for more than 2 months (Gibbs *et al.,* 2005) and where longer storage periods are necessary (e.g. due to site accessibility for land spreading) this only tends to be up to a maximum of 6-8 months. Changes in the composition, and particularly the potential for decomposition, will

vary with the type of PS material with chemical/physically treated sludges likely to be more stable than biological treated materials.

Figure 3.13 E-coli numbers in water draining from the PS storage heaps



4. Discussion of research questions

1. How do physical and chemical properties of soil and pore water change over time?

There was very little change (*P*>0.05) in soil properties between the site characterisation sampling of the control and fresh PS treatment in September 2014 and in April 2014, *c.*6 months after application of PS, with any significant changes (notably total C and conductivity, which increased over time; *P*<0.01), occurring on the plots of both treatments, and therefore attributable to variations in sampling or analysis. Differences in topsoil extractable Mg concentrations measured at the outset of the experiment, prior to fresh PS additions, were still apparent at Gleadthorpe. Likewise, the differences in extractable K concentrations were also still apparent at Harper Adams and can be attributed to background soil variability.

Insufficient pore water could be extracted from the soils for any meaningful analyses to be performed due to the inherently low water retention on these sandy soils.

2. How do physical and chemical properties of soil and pore water in plots with application of paper sludge compare to control plots?

There was a small (*c.*0.3-0.6 pH units), but not statistically significant (*P*>0.05) increase in topsoil pH *c.*6 months following the addition of fresh PS material, relative to the untreated control. However, overall a single 30 t/ha application of PS had very little effect (*P*>0.05) on topsoil chemical properties (Table 3.2Table 3.3), microbial biomass and aggregate stability (Table 3.4). This was not surprising as it has been shown that repeated and relatively large organic material additions are needed to produce measurable changes in soil properties (Bhogal *et al.,* 2009; 2011). Indeed, previous sampling of the historic PS treatments at Gleadthorpe and Harper Adams experimental sites undertaken as part of the SOIL-*QC* experimental programme in 2006/07 (Defra, 2011) concluded that even after 2-3 years of repeated PS additions (supplying *c.*10-12 t/ha organic carbon) changes in soil properties (particularly soil physical properties) were small and difficult to detect.

The characterisation sampling of the historic PS treatment plots in comparison to the untreated control in January 2013 therefore provided valuable information on the longer-term effects of repeated PS additions, although only a limited number of analyses were common to the sampling undertaken in 2006/07 (notably pH, total C and microbial biomass). Here 6 to 9 years of annual applications at rates varying between 30 and 75 t/ha (fresh weight) and supplying up to 32 t/ha C, resulted in a clear demonstration of the value of PS as a liming material as well as a soil conditioner.

After 2-3 years of PS addition in 2006/07 the topsoil pH had increased by 0.5-1.0 units, whereas after 6-9 years of repeated addition this difference had increased to *c*.2 pH units, with a pH of *c*.7.8 measured at both sites, relative to the untreated control at pH 5.7-6.0 (Figure 3.1). The carbon inputs associated with the PS additions up to 2006/07 resulted in a small increase in topsoil C at both sites (Figure 3.2). Over the following 5-6 years a further 15-20 t/ha C was applied with the repeated PS additions, resulting in further increases in topsoil C (P<0.05; Figure 3.2) equating to *c.*6-8 t/ha additional C in the topsoil, and associated with an increase in soil microbial biomass (Figure 3.3).

The SOIL-*QC* research demonstrated that repeated additions of organic materials over a 10-15 year timescale (supplying up to 100 t/ha C) resulted in improvements in not only soil C and microbial biomass, but also soil physical properties such as plant available water capacity, porosity, density and strength (Bhogal *et al.,* 2009; Defra, 2011). It is therefore likely that repeated addition of PS materials over the longer term (>10 years) will lead to similar benefits. Depending on alternative uses of PS, application to land is likely to be beneficial for increasing soil C storage for the mitigation of climate change (Powlson *et al.,* 2012).

There was very little effect of the repeated PS additions on topsoil metal concentrations. Only topsoil strontium concentrations increased relative to the untreated control (P<0.05), although concentrations were low and well within the range of reported values for typical agricultural soils (Rawlins *et al*., 2012). This confirms earlier work by Gibbs *et al* (2005) where the impact of heavy metal additions on human and animal health was considered to be very low in the short-term and similar to, or lower than, other organic materials applied to agricultural land in the long term.

Insufficient pore water could be extracted from the soils for any meaningful analyses to be performed, due to the inherently low water retention on these sandy soils.

3. To what extent are PCOCs taken up by crops grown with application of paper sludge?

There was no significant effect of a single fresh PS application on the uptake of PCOCs by winter wheat or spring barley. Gibbs *et al* (2005) suggest that the uptake of certain metals may be decreased following PS additions due to a reduction in solubility with increasing soil pH. Within the scope of this study these results therefore suggest that PS application has no significant detrimental impact on human and animal health in the short-term due to the uptake of PCOCs by cereal crops grown on sandy soils under temperate climatic conditions.

4. How does uptake of PCOCs by crops grown with application of paper sludge compare to uptake by crops grown in control plots?

There was no significant effect of a single fresh PS application on the uptake of PCOCs by winter wheat or spring barley which suggests that, within the scope of this study, PS application has no detrimental impact on human and animal health in the short-term due to plant uptake of PCOCs.

5. How does the total soil microbial biomass change over time in soils with application of paper sludge?

The microbial biomass is very dynamic in soil and responds to weather, carbon input and season (Rice *et al.,* 1996). The size of the microbial biomass is therefore subject to soil moisture and temperature conditions at the time of sampling as well as plant dynamics and it is generally

recommended that samples are taken at the same time in early spring or late autumn in temperate regions (Rice *et al.,* 1996). At Gleadthorpe microbial biomass C was *c.*30 mg/kg lower in April 2014 than in September 2013 (prior to PS application) on both the control and fresh PS treatments, most likely due seasonal variation in soil moisture and temperature.

At Harper Adams, microbial biomass C remained relatively constant over this time period (158 mg/kg in September 2013 and 153 mg/kg in April 2014). However data from the historic PS applications does show that repeated applications of PS over 6-9 years results in an increase the total soil microbial biomass (Bhogal *et al.,* 2009; 2011).

6. How does the total soil microbial biomass in soils with application of paper sludge compare with total soil microbial biomass in control plots?

There was no significant effect of a single application of fresh PS on topsoil microbial biomass, relative to the untreated control. However, where PS had been applied annually for 6-9 years (on the historic PS treatment) topsoil microbial biomass increased *c.*2 fold at Gleadthorpe and *c.*1.5 fold at Harper Adams (Figure 3.3 and Figure 3.4). Measurements of soil microbial biomass size i.e. C and N contents, provide an indication of a soil's ability to store and recycle nutrients and energy, such that a higher soil microbial biomass generally indicates a 'better' soil quality (Dick, 1992). The results at both EQual sites therefore suggest that repeated PS applications can result in an improvement in soil biological functioning and quality.

7. How do storage durations affect key properties of the paper sludge (e.g. nutrient content, pH, pathogens)?

Over the course of the *c.*12month storage period the total weight of PS material within each of the storage heaps decreased by *c.*25%, equivalent to a loss of *c.*1.25 tonnes. This was most likely due to decomposition (oxidation) of the organic fraction of the PS material, with both the total C and organic matter content decreasing during the course of the 12 month storage period (Figure 3.3 and Figure 3.6). Although there was some variability in the concentration of other nutrients and metals throughout the storage period the only consistent variation was for total sulphur, which decreased to negligible concentrations over the *c.*12 month period, and total manganese and strontium whose concentrations increased by 10-15% ($P<0.01$). *E.coli* was present at the start of the storage period, possibly due to the presence of some biologically treated material within the batch of PS, but after just 1 month of storage these had died off in line with similar work undertaken with farm manures (Nicholson *et al.*, 2005).

The majority of paper mills would not be expected to store PS on site for more than 2 months, and where longer storage periods are necessary (e.g. due to site accessibility for land spreading) this only tends to be up to a maximum of 6-8 months. Changes in the composition, and particularly the potential for decomposition of stored materials is likely to vary with the type of PS material, particularly if it contains biologically treated materials. The growth of weeds on uncovered heaps is likely to be a problem if materials are stored over the spring and summer.

If heaps are left uncovered for extended periods over the winter months, then there is the potential for the generation of leachate containing elevated concentrations of multiple pollutants (e.g. nitrate-N, ammonium-N, phosphorus-P, BOD and *E-coli*), which could cause detrimental effects if they reached surface water bodies in an undiluted form. However, the total load of such nutrients is likely to be low (<5% of the total within the heap) and well below (i.e. less than a tenth) those measured from solid manure heaps, in particular for nitrogen/nitrate, phosphorus, BOD and *E-coli* (Nicholson *et al.*, 2013). In practice, pollutants in leachates infiltrating soil underneath a field heap of PS or in runoff from the heap are likely to be either retained in the soil or will mix and be diluted with runoff from the rest of the field.

However, the results demonstrate the importance of following good practice guidelines for the storage of PS materials to minimise the risk of pollutant losses to the environment (Anon, 2009; CPI, 2014). The recently revised Code of Good Practice for Landspreading Paper Mill Sludges (CPI, 2014) also gives clear guidance on best practice, emphasising the need to liaise with farmers regarding the suitability of sites for spreading and giving guidance on contingency planning for longer-term storage of PS when extreme weather conditions prevent spreading.

8. How do the yields of crops grown with application of paper sludge compare with those grown in control plots?

Although winter wheat and spring barley grain yields increased by *c*.1.4 t/ha and *c*.0.2 t/ha following fresh PS treatment at Gleadthorpe and Harper Adams, respectively (Table 3.5), these increases were not statistically significant ($P>0.05$). They most likely reflect the additional manufactured fertiliser N that was applied to the fresh PS treatment, to counter potential N immobilisation following the PS additions.

Many studies have shown that the application of paper sludge can decrease crop N availability via immobilisation ('lock-up') of N into the microbial biomass due to the high C:N ratio of the applied PS material (particularly for non-biologically treated paper sludges), Gibbs *et al.,* (2005). However, the C:N ratio of the PS material is not necessarily an accurate guide to the potential N immobilisation. Further research to understand N lock up and potential re-release following the land spreading of different PS materials would be beneficial.

5. Conclusions

The PS field trials demonstrated no significant negative effect on a range of soil chemical, physical and biological properties or on the uptake of potential substances of concern by cereal crops, suggesting that a single application of PS to agricultural soils presented no unacceptable environmental or human health risks. However, further work over longer time periods and higher application rates would be required in order to fully understand any potential risks. Here, the study benefitted from the historic PS treatment which had received repeated application of PS over several years and provided a useful dataset.

Together with earlier sampling undertaken as part of the SOIL-QC experimental programme, clearly demonstrated the agricultural benefit of PS as a valuable liming material and soil conditioner leading to an increase in topsoil organic matter and soil biological functioning. However, it is important that adequate manufactured fertiliser N is applied in order to account for potential N immobilisation following PS application so that crops do not become N-limited and yields are not impaired.

The EQual PS field trials furthered understanding of the environmental impact and agricultural benefits of the application of PS to agricultural soils. The study also highlighted the importance of following good agricultural practice when storing PS materials in temporary field heaps in order to avoid potentially harmful leachate reaching surface water bodies in an undiluted form. The results from this study will be useful for informing future QRAs on the storage and land-spreading of PS. The objectives for the EQual PS field trials have therefore been achieved.

6. Acknowledgements

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8. List of abbreviations

ANOVA	Analysis of Variance
BOD	Biological Oxygen Demand
PCOC	Potential Chemicals of Concern
FACTS	Fertiliser Advisers Certification and Training Scheme
GT	Gleadthorpe experimental site
HA	Harper Adams experimental site
MOP	Muriate of Potash
NLS	National Laboratory Service
PLA	Poultry Litter Ash
PS	Paper Sludge
TNV	Total Neutralising Value
TSP	Triple Super Phosphate

Appendix 1: Field Study Method Statements

EQual Project (30636) Method Statement:
Baseline Soil Sampling & Analysis

This method statement details the procedures to be followed in soil sampling the two EQual experimental sites (ADAS Gleadthorpe and Harper Adams Agricultural College) at the outset of the study.

In order to characterise the site 'baseline' topsoil samples (0-15cm) should be taken from each plot at Gleadthorpe prior to any treatment applications. At Harper Adams samples should only be taken from the untreated control, poultry litter ash (PLA) and fertiliser treatments (i.e. excluding the paper sludge (PS) treatment).

Equipment

- Soil sampling for the chemical analyses will be taken using a hand-held "Cheese" corer. This is suitable for most soil conditions.
- A spade or trowel for aggregate stability sampling.
- Soil spatula, for use with cheese corer.
- Ruler graduated in cm.
- New clean polythene bags 300 x 200 mm to 500 x 400 mm, labelled accordingly.
- Rubber bands or ties (or use self-seal bags).
- Boxes for storage of samples.
- 1kg plastic tubs (supplied by NLS).
- 1 litre glass jars.
- Experiment site plan.

Sampling Procedures

The following samples should be taken when the soil is moist, but not frozen or too wet:

- Soil samples from 0-15cm depth will be taken following the methodology detailed in the "Fertiliser Manual (RB209)" (Defra, 2010; Appendix 3). Twenty soil core samples will be taken at even intervals in a 'W' shape pattern across each plot, using a hand held "Cheese corer", giving the specified volume of soil. The soil from each plot will be collected in one bag to generate one composite (representative) sample from each plot. Samples should be placed in 1 kg plastic tubs (3 per plot) and sent, fresh, in cool boxes to the NLS laboratory (store in a fridge at <4°C prior to dispatch).

- A further *c.*1kg of topsoil (0-15cm) will be collected according to the methodology detailed in the "Fertiliser Manual (RB209)" (Defra, 2010) for the determination of soil microbial biomass C & N. Twenty soil core samples will be taken at even intervals in a 'W' shape pattern across each plot, using a hand held "Cheese corer". The soil from each plot will be collected in one bag to generate one composite (representative) sample from each plot. Samples should be placed in plastic bags and sent, fresh, in cool boxes to the ADAS laboratory at Boxworth (F.A.O. Helen Kingston/Masuma Chauhan). Store in a fridge at <4°C prior to dispatch.

- Using a trowel/spade, twenty topsoil (0-15cm) samples will be taken from each plot spread evenly in a 'W' shape pattern to provide *c.*1.0kg of bulked fresh soil sample per plot. The soil sample should be sent to the ADAS laboratory at Boxworth (F.A.O. Helen Kingston/Masuma Chauhan) for the determination of aggregate stability. Care should be taken when sampling, and during transit of these samples, in order to minimise disruption

of the soil aggregates. Samples should be sent to the laboratory in boxes and should not be stacked on top of each other.

- A further *c.*1kg topsoil (0-15cm) will be taken following the methodology detailed in the "Fertiliser Manual (RB209)" (Defra, 2010) for storage in the sample archive at ADAS Gleadthorpe. Samples should be stored in 1 litre glass jars.

Labelling

All samples will be labelled using the following method:

EQual YAS2002/SITE/PLOT NUMBER/DATE

Samples will not be dispatched on a Friday, as they may deteriorate over the weekend. Samples will be stored in a fridge (<4°C) prior to transit.

Roles and Responsibilities

Sampling is to be conducted by a team led by the Site Manager

Data Recording

An entry will be made in the experimental diary to record the date and time of soil sampling, weather and ground conditions, plots that were sampled, sampler name and laboratory dispatch date and details.

Health and Safety

- There is a risk of contracting tetanus from soil. Anyone who takes soil samples should ensure they maintain a course of injections to protect themselves against tetanus infection.
- Efficient soil sampling tools have sharp edges; care should be taken when they are used.
- Back injuries can occur when using soil sampling tools. This risk can be minimised by using a good lifting technique, i.e. keep the back straight and bend the knees.
- The site specific risk assessment at each experimental location (which already considers soil sampling) will be consulted before and after sampling. If any amendments are required the risk assessment will be updated.

References

Defra (2010). The Fertiliser Manual (RB209) 8th edition. The Stationery Office, Norwich

EQual Project (30636) Method Statement:
Microbial Biomass Carbon and Nitrogen Analysis

This method statement details the procedures to be followed in determining the microbial biomass carbon (C) and nitrogen (N) content of soil sampled from the two EQual experimental sites (ADAS Gleadthorpe and Harper Adams University) in February 2013 ('baseline'), March/April 2013 ('year 1') and March/April 2014 ('year 2').

Microbial biomass C & N will be determined at ADAS Boxworth using the fumigation-extraction method (Jenkinson & Powlson, 1976; Wu *et al*., 1990), with extracts sent to NRM laboratories for analysis. Extractions will be performed within 3 months of receipt of the soil samples.

Equipment

- 6.25mm mesh sieve.
- Tissue/Cotton wool.
- Incubator set at 25 °C.
- 250ml plastic screw-top bottles.
- 60/100ml glass jars or beakers.
- Dry matter tins & oven.
- Desiccator.
- Fume cupboard.
- Vacuum pump.
- Reciprocal shaker.
- 30ml sample bottles.
- 15cm Whatman GF/A filter papers.

Reagents

- Soda Lime (1.0-2.5mm, non-hygroscopic granules).
- Ethanol-free Chloroform ($CHCl_3$).
- 0.5M Potassium sulphate (K_2SO_4).
- Anti-bumping granules (fused alumina).

Analysis Procedure

Biomass C & N should be determined on soils at 50% water holding capacity – WHC (± 2%). Therefore, upon receipt of the samples the gravimetric moisture content must be determined immediately and WHC adjusted accordingly. The method used to determine soil microbial biomass C & N is that of Jenkinson & Powlson (1976) and Wu *et al. (*1990). Chloroform is used to fumigate a soil sample and kill the soil microbial population, resulting in the release of microbial C and N. This is extracted using potassium sulphate solution, with the extracts analysed for total organic C and N (at NRM laboratories). Biomass C & N can then be calculated from the difference in organic C and N extracted from fumigated and unfumigated soil samples. The analysis must be performed within 3 months of receipt of the soil samples, with extracts sent to NRM laboratories within 48 hours of extraction. All samples (soils and extracts) will be stored in a fridge (< 4 °C) prior to analysis. A 1 litre sample of blank K_2SO_4 will be sent to NRM laboratories with each batch of samples for matrix matching.

Labelling

All samples will be labelled using the following method:

EQual YAS2002/SITE/PLOT NUMBER/DATE

Samples will not be dispatched to NRM laboratories on a Friday, as they may deteriorate over the weekend. Samples will be stored in a fridge (<4°C) prior to transit.

Roles and Responsibilities

Extraction is to be conducted by a team led by the Laboratory Manager at ADAS Boxworth.

Data Recording

An entry will be made in the experimental diary to record the date of analysis and analyst, as well as the NRM laboratory dispatch date and details. Data will be recorded electronically (example spreadsheet in Appendix 1).

Health and Safety

- There is a risk of contracting tetanus from soil. Anyone who takes soil samples or working with soil should ensure they maintain a course of injections to protect themselves against tetanus infection. Protective clothing (e.g. goggles, gloves, laboratory clothing) should be worn and hands washed before eating, drinking or smoking.

- Chloroform is classified as a harmful product which can cause serious damage to health by prolonged exposure through inhalation and if swallowed. It is essential that its use is confined to an efficient fume cupboard and that eye protection and gloves are worn when handling this substance.

- Soda lime is 75% $Ca(OH)_2$ and 3.5% NaOH (the balance is water), which is a caustic irritant if dust is inhaled, or contact made with eyes or broken skin. It is essential that gloves and eye protection are worn when handling this substance.

- A laboratory risk assessment for each analytical procedure is currently in place and will be consulted before and after analysis. If any amendments are required the risk assessment will be updated.

References

Jenkinson, D.S. & Powlson, D.S. (1976) The effect of biocidal treatments on metabolism in soil. V. A method for measuring soil biomass. *Soil Biology and Biochemistry,* **8**, 209-213.

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Example excel spreadsheet for the recording and calculation of soil microbial biomass C and N

Filename:

MEASUREMENT OF MICROBIAL BIOMASS

PROJECT CODE:
PROJECT TITLE:
SITE:
DATE SAMPLES TAKEN:
NUMBER OF SAMPLES:

Received at Boxworth: **Name:** **Date:** **Blank TOC mg/l:**
Where stored at Boxworth: **Name:** **Date:** **Blank TN mg/l:**
Soils Processed **Name:** **Date:**
Extracts to NRM labs **Name:** **Date:**

Correction factors for conversion of EN or EC to BN or BC:

TOC : Shimadzu TOC-VCPH analyser: KC = 0.45 (2.22)
Npers: UV persulphate oxidation: KN = 0.45 (2.22)

		Results from NRM laboratories													
Sample ID/Plot	Sample Type	TN in 0.5M K2SO4 mg/l	TOC mg/l in 0.5M K2SO4	net TN in 0.5M K2SO4 mg/l	net TOC mg/l in 0.5M K2SO4	%SMC	DW Soil	Vol. Extract used (ml)	N (mg/kg)	TOC (mg/kg)	Nitrogen (EN) (mg/kg)	Carbon (EC) mg/kg	Biomass N (BN) mg/kg	Biomass C (BC) mg/kg
	Extraction			0.00	0.0		50	200	0.0	0.0	0.0	0.0	0.0	0.0
	Fumigation													
	Extraction													
	Fumigation													

EQual Project (30636) Method Statement:
Aggregate Stability Analysis

This method statement details the procedures to be followed in determining the aggregate stability of soil sampled from the two EQual experimental sites (ADAS Gleadthorpe and Harper Adams University) in February 2013 ('baseline'), March/April 2013 ('year 1') and March/April 2014 ('year 2').

Soil aggregate stability will be determined at ADAS Boxworth, using the dispersion ratio method of aggregates in the size range 10 – 20mm (Anon, 1982).

Equipment

- Air dried sample of soil aggregates in the size range 10-20mm.
- Plastic measuring cylinders, volume 1000 ml.
- Laboratory film (100 mm wide Nescofilm).
- 20 ml pipette grade B.
- Rubber bands (2 per measuring cylinder).
- Balance with a resolution of 0.01 g or better.
- Balance with a resolution of 0.0001 g or better.
- 50 ml glass beakers 2 per sample plus 1 extra.
- Dedicated electrically operated end over end shaker (developed by ADAS).
- Temperature controlled environment at 20°C ± 2°C.
- Vacuum desiccator containing active silica gel.
- Stopwatch.
- Thermometer.
- Calgon dispersant (50g sodium hexametaphosphate and 7g anhydrous sodium carbonate in dissolved in distilled water and made up to 1 litre).
- Proforma sheet for data recording (example attached).

Analysis Procedure
The method used to determine aggregate stability is described by Anon (1982). This method compares the proportion, by weight, of silt and clay suspended by mild slaking forces to the total amount present in the sample. The test should be carried out in a temperature-controlled environment, since the rate at which particles settle out of suspension depends upon the temperature of the fluid.

Labelling
All samples will be labelled using the following method:

EQual YAS2002/SITE/PLOT NUMBER/DATE

Roles and Responsibilities
Analysis is to be conducted by a team led by the Laboratory Manager at ADAS Boxworth.

Data Recording
An entry will be made in the experimental diary to record the date of analysis and Analyst. The proforma in Appendix 1 will be used to record the results. Results will be manually transferred to an excel workbook and independently checked.

Health and Safety

- There is a risk of contracting tetanus from soil. Anyone who takes soil samples or working with soil should ensure they maintain a course of injections to protect themselves against tetanus infection. Protective clothing (goggles, gloves, laboratory clothing) should be worn and hands washed before eating, drinking or smoking.
- Instruments will only be operated by a trained member of the laboratory staff.
- A laboratory risk assessment for each analytical procedure is currently in place (which already considers aggregate stability) and will be consulted before and after analysis. If any amendments are required, the risk assessment will be updated.

References
Anon. (1982). *Techniques for Measuring Soil Physical Properties*. MAFF Reference Book 441. HMSO, London.

RECORD OF THE DETERMINATION OF SOIL STABILITY BY THE DISPERSION RATIO TEST

0.01 g Balance serial No.....checked*				0.0001 g Balance serial No..... checked*				Weight of beaker A	Weight of beaker A + calgon residue	Weight of calgon residue (a)
YES		NO		YES		NO				

Aggregate size used	1 - 2 mm*	< 2 mm*	Other please specify

Shaker calibration checked*		No. of inversions/minute set.
YES	NO	

* tick box

		Gentle Dispersion			Complete Dispersion			Dispersion
Lab No	Replicate No	Weight of beaker	Weight of beaker + residue	Weight of residue (b)	Weight of beaker	Weight of beaker + residue	Weight of residue (c)	Ratio
	1							
	2							
	3							
	1							
	2							
	3							
	1							
	2							
	3							
	1							
	2							
	3							
Recorded by and date								

Certified by..... Location.....

EQual Project (30636) Method Statement:
Treatment Application: paper sludge

This method statement details the procedures to be followed when applying paper sludge (PS) at the two EQual experimental sites (ADAS Gleadthorpe and Harper Adams University College) in September/October 2013.

All treatments will be applied by hand at the same time at each experimental site (as far as practically possible). During application, samples of the material will be collected for laboratory analysis and archiving.

Equipment

- Platform or spring balance to weigh up to 100kg.
- Dustbins or polythene sheets.
- 10 litre buckets.
- Garden forks.
- String and pegs.
- New clean polythene bags 300 x 450 mm, labelled accordingly.
- Rubber bands or ties.
- Boxes for storage of samples.
- 1 litre glass jars.
- Experiment site plan.

Application Procedures

PS will be applied in accordance with good agricultural practice (Defra, 2009; Defra, 2010) i.e. not when the soil is waterlogged or frozen, or if heavy rain is expected within 24 hours following application. The storage and use of PS must adhere to the requirements of the EA Regulatory Position Statement.

- PS will be applied at the rate agreed with the EA Project Manager: 30 t/ha (fresh weight).

- Weigh the amount of PS required for each plot, using the platform or spring balance, and transport to the plot in dustbins or on polythene sheets prior to application.

- Using string and pegs to mark out the plot boundaries.

- Apply the PS evenly using a garden fork at the determined application rate, breaking up large blocks. Take representative samples of PS (*see section below*).

- Once applied, remove treatment markers and wash/disinfect all contaminated equipment and protective clothing.

Incorporation Procedures

The PS will be applied to the stubble of the previous crop and will be soil incorporated (to *c*. 20cm) prior to crop establishment. The method of soil incorporation (plough, tine or discs) will be in accordance with best practice for the site/soil type and will depend on ground conditions at the time of application and subsequent cropping.

Sampling Procedures

Each year during PS application, representative samples will be taken for laboratory analysis at NLS and archiving at Gleadthorpe, in accordance with the EA project specification '30636 EQual programme agriculture field trials Jan 2013':

- During the application of PS, subsamples will be collected from each plot (3 plots in total) and placed in a polythene bag to make up *c.*2 kg of material per plot. Samples taken from the Harper Adam's site should be sent to Gleadthorpe for processing. In addition, 300g of the PS applied to each plot should be placed in sterile polypropylene jars for immediate submission to NLS for e-coli and salmonella analysis.

- At Gleadthorpe each 2kg sample will be split with *c.*1kg sent to NLS in labelled tubs for the adapted BioCompost analysis suite, *c*.120g (50g minimum) placed in labelled glass jars and sent to NLS for organic C analysis and all remaining material stored in glass jars for archiving. All samples will be stored in a cold store (<4°C) prior to submission to the laboratories.

- Samples will be sent to NLS using overnight couriers. Archived samples will remain in the cold store at Gleadthorpe.

Labelling

Samples will be labelled for submission to NLS as detailed in the table below:

Label	Description
HAPSFPSF-1	Fresh paper sludge applied to block 1 at Harper Adams
HAPSFPSF-2	Fresh paper sludge applied to block 2 at Harper Adams
HAPSFPSF-3	Fresh paper sludge applied to block 3 at Harper Adams
GTPSFPSF-1	Fresh paper sludge applied to block 1 at Gleadthorpe
GTPSFPSF-2	Fresh paper sludge applied to block 2 at Gleadthorpe
GTPSFPSF-3	Fresh paper sludge applied to block 3 at Gleadthorpe

Additionally, the label should include the date of sampling.

Samples will not be dispatched on a Friday, as they may deteriorate over the weekend. Samples will be stored in a fridge (<4°C) prior to transit.

Roles and Responsibilities

Application and sampling of PS is to be conducted by a team led by the Site Manager.

Data Recording

An entry will be made in the experimental diary to record the date and time of application and sampling, plots that PS was applied to, application rates, weather and ground conditions at the time of application, sampler name and laboratory dispatch date and details.

Health and Safety

- Avoid getting the material on the skin, but if this happens wash it off as soon as possible. Wash hands and forearms thoroughly before handling food, drinking or smoking.

- Leptospirosis (Weil's disease), a serious and sometimes fatal infection is transmitted to humans by contact with urine from infected rats. As rats often scavenge organic material stores, take precautions as specified in HSE Agriculture Information Sheet no. 2.

- Handling organic material may expose workers to other serious infectious diseases. These include poliomyelitis, tetanus, typhoid fever, hepatitis A and hepatitis B. See Occupational Health Service Notice 93/6.

- Wear waterproof boots, waterproof jacket, trousers and gauntlets or long gloves, when sampling organic materials. Wear a face shield where splashing of material may occur. Wear a dust mask or preferably an airstream helmet when sampling dusty materials.

- Ensure that the outside of sample bags and containers are clean and free from contamination so that reception staff at the laboratory are not exposed to biohazards.

- The site specific risk assessment at each experimental location (which already considers organic material application and sampling) will be consulted before and after application. If any amendments are required, the risk assessment will be updated.

References

Defra (2009). *Protecting our Water, Soil and Air: A Code of Good Agricultural Practice for Farmers, Growers and Land Managers.* The Stationery Office, Norwich.

Defra (2010). *The Fertiliser Manual (RB209).* The Stationery Office, Norwich

EQual Project (30636) Method Statement:
Annual Soil Sampling & Analysis

This method statement details the procedures to be followed as part of the annual soil sampling programme at the two EQual experimental sites (ADAS Gleadthorpe and Harper Adams Agricultural College) during the study.

In Spring (March/April) 2013 & 2014 topsoil samples (0-15cm) will be taken from each plot at both experimental sites prior to the main manufactured fertiliser N applications and analysed to identify any treatment effects on selected soil and pore water properties.

Equipment

- Soil sampling for the chemical analyses will be taken using a hand-held "Cheese" corer. This is suitable for most soil conditions.
- A spade or trowel for aggregate stability sampling.
- Soil spatula, for use with cheese corer.
- Ruler graduated in cm.
- New clean polythene bags 300 x 200 mm to 500 x 400 mm, labelled accordingly.
- Rubber bands or ties (or use self-seal bags).
- Boxes for storage of samples.
- 1kg plastic tubs (supplied by NLS).
- 1 litre glass jars.
- Experiment site plan.

Sampling Procedures

The following samples should be taken when the soil is moist, but not frozen or too wet:

- Soil samples from 0-15cm depth will be taken following the methodology detailed in the "Fertiliser Manual (RB209)" (Defra, 2010; Appendix 3). Twenty soil core samples will be taken at even intervals in a 'W' shape pattern across each plot, using a hand held "Cheese corer", giving the specified volume of soil. The soil from each plot will be collected in one bag to generate one composite (representative) sample from each plot. Samples should be placed in 1 kg plastic tubs (3 per plot) and sent. Fresh. in cool boxes to the NLS laboratory (store in a fridge at <4°C prior to dispatch).

- A further *c.*1kg of topsoil (0-15cm) will be collected according to the methodology detailed in the "Fertiliser Manual (RB209)" (Defra, 2010) for the determination of soil microbial biomass C & N. Twenty soil core samples will be taken at even intervals in a 'W' shape pattern across each plot, using a hand held "Cheese corer". The soil from each plot will be collected in one bag to generate one composite (representative) sample from each plot. Samples should be placed in plastic bags and sent, fresh, in cool boxes to the ADAS laboratory at Boxworth (F.A.O. Helen Kingston/Masuma Chauhan). Store in a fridge at <4°C prior to dispatch.

- Using a trowel/spade, twenty topsoil (0-15cm) samples will be taken from each plot spread evenly in a 'W' shape pattern to provide *c.*1.5kg of bulked fresh soil sample per plot. The soil sample should be sent to the ADAS laboratory at Boxworth (F.A.O. Helen Kingston/Masuma Chauhan) for the determination of aggregate stability. Care should be taken when sampling and during transit of these samples, in order to minimise disruption of the soil aggregates. Samples should be sent to the laboratory in boxes, and should not be stacked on top of each other.

- A further *c.*1kg topsoil (0-15cm) will be taken following the methodology detailed in the "Fertiliser Manual (RB209)" (Defra, 2010) for storage in the sample archive at ADAS Gleadthorpe. Samples should be stored in 1 litre glass jars.

Labelling

All samples will be labelled using the following method:

EQual YAS2002/SITE/PLOT NUMBER/DATE

Samples will not be dispatched on a Friday, as they may deteriorate over the weekend. Samples will be stored in a fridge (<4°C) prior to transit.

Roles and Responsibilities

Sampling is to be conducted by a team led by the Site Manager.

Data Recording

An entry will be made in the experimental diary to record the date of soil sampling, weather and ground conditions, plots that were sampled, sampler name and laboratory dispatch date and details.

Health and Safety

- There is a risk of contracting tetanus from soil. Anyone who takes soil samples should ensure they maintain a course of injections to protect themselves against tetanus infection.
- Efficient soil sampling tools have sharp edges; care should be taken when they are used.
- Back injuries can occur when using soil sampling tools. This risk can be minimised by using a good lifting technique, i.e. keep the back straight and bend the knees.
- The site specific risk assessment at each experimental location (which already considers soil sampling) will be consulted before and after sampling. If any amendments are required, the risk assessment will be updated.

References

Defra (2010). The Fertiliser Manual (RB209) 8th edition. The Stationery Office, Norwich

EQual Project (30636) Method Statement:
Harvest – Grain/seed yield & analysis

This method statement details the procedures to be followed for harvesting the two EQual experimental sites (ADAS Gleadthorpe and Harper Adams Agricultural College) in August 2013 & 2014 for the determination of crop yield, dry matter content, nutrient offtake and uptake of heavy metals and organic contaminants.

Materials and Equipment

- Experiment site plan.
- Record sheet and pen.
- Polypropylene screw top bottles of 1 litre capacity, labelled accordingly.
- A plastic stacking tray or other suitable container to store the bottles whilst harvesting is in progress.
- Dust mask and safety glasses or Airstream helmet (for operators not protected by a cab).
- Ear plugs.

Harvesting and Sampling Procedure

Harvesting of plots will take place in line with good agricultural practice (Defra, 2009; Defra, 2010) i.e. when the soil is dry enough to support the weight of a combine thus reducing the risks of damaging the soil structure and causing compaction. A small plot combine will be used, driven by an experienced member of staff. Record the weight of grain harvested from each plot and the harvest area (plot length x harvest width).

During harvesting, *c.*1 kg samples of the grain from each individual plot will be collected in a 1 litre polypropylene screw top bottle labelled accordingly. Take the sample by gradually filling the bottle from the flowing grain sample 'little and often'.

Prior to dispatching all grain/seed samples to the laboratory for analysis, a *c*. 100g sub-sample should be taken from each plot for immediate dry matter determination (by drying a known weight of sample for 24 hours at 100°C; the dry matter content is then calculated from the difference in weight between the fresh and dry grain/seed sample). The remaining grain will be sent to NLS to analyse the grain nutrient, metal and organic contaminant concentrations.

Labelling

All samples will be labelled using the following method:

EQual YAS2002/SITE/PLOT NUMBER/DATE

Roles and Responsibilities

Harvesting is to be conducted by a team led by the Site Manager.

Data Recording

An entry will be made in the experimental diary to record the date of harvesting, weather and field conditions, sampler name and laboratory dispatch date and details.

The weight of grain harvested from each plot, together with the harvest area (plot length x harvested width), should be recorded on a standard proforma (Appendix 1).

Health and Safety

- Most combines in use in ADAS have cabs for the driver, but in some cases the operator(s) is/are exposed. In the absence of cab protection operators should wear an approved dust mask with protective glasses or an air-stream type helmet. The Health & Safety Executive Agricultural Sheet No 3 gives the maximum exposure limit for grain dust as specified in the Schedule of COSHH Regulations 1988.

- Combine harvesters are noisy when operating; wear either approved ear plugs or ear muffs where noise is above recommended exposure levels

- A site specific risk assessment for each experimental location is currently in place (which already considers harvesting) and will be consulted before and after analysis. If any amendments are required the risk assessment will be updated.

References

Defra (2009) *Protecting our Water, Soil and Air: A Code of Good Agricultural Practice for Farmers, Growers and Land Managers.* The Stationary Office, Norwich.

Defra (2010). The Fertiliser Manual (RB209) 8th edition. The Stationery Office, Norwich

Standard record proforma

ADAS GLEADTHORPE

Scale weight checked

Trial no. ..... Year :-..... G.S.:-..... Sheet ..... of .....

Site:- ..... S.O.P. no :- ..... Date :- .....

Obs./Assessment :- .....

Area/Unit/Scale :- .....

M=mistake in recording
C=calculation error
P=recorded in wrong place
T=transcription error
CH= e.g. checked(unusual result has been checked)
E=error explained elsewhere

Plot													
1													
2													
3													
4													
5													
6													
7													
8													
9													
0													
1													
2													
3													
4													
5													
6													
7													
8													
9													
0													

Balance I.D. no.
Drying oven I.D. no.

Recorded by:-
Date:-

Certified by:-
Date:-

d:\data\crops\2011\record.xls

Appendix 2: Experimental site diaries and fertiliser inputs

Gleadthorpe experimental diary and fertiliser policy

Activity	Date
Site characterisation soil sample (control & historic PS)	28/1/13
5 t/ha lime and 100 kg/ha K_2O applied to all treatments; 40 kg/ha N applied to historic PS treatment	7/2/13
Spring barley drilled	8/4/13
40 kg/ha N and 50 kg/ha SO_3 applied to all treatments	15/4/13
70 kg/ha N and 3 kg/ha $MnSO_4$ applied to all treatments	4/5/13
30 kg/ha N applied to historic PS treatment only	23/5/13
3 kg/ha $MnSO_4$ applied to all treatments	1/6/13
3 kg/ha $MnSO_4$ applied to all treatments	25/6/13
Spring barley harvested	5/9/13
Site characterisation soil sample (control & fresh PS)	20/9/13
Application and incorporation of fresh PS	12/11/13
Winter wheat drilled	2/12/13
100 kg/ha K_2O applied to all treatments, 40 kg/ha N applied to the control and 80 kg/ha applied to the fresh and historic PS treatments	20/2/14
Annual soil sample	28/4/14
60 kg/ha N, 50 kg/ha SO_3 and 4.5 kg/ha MnSO4 to all treatments	29/4/14
60 kg/ha N and 2.5 kg/ha MnSO4 to all treatments	15/5/14
Winter wheat harvested	13/8/14

Harper Adams experimental diary and fertiliser policy

Activity	Date
Site characterisation soil sample (control & historic PS)	30/1/13
40 kg/ha N, 75 kg/ha K_2O and 40 kg/ha SO_3 applied to all treatments	3/4/13
70 kg/ha N applied to all treatments	26/4/13
70 kg/ha N applied to control; 105 kg/ha to the historic PS treatment	16/5/13
Winter wheat harvested	21/8/13
Site characterisation soil sample (control & fresh PS)	10/9/13
Application and incorporation of fresh PS	7/10/13
Spring barley drilled	13/3/13
110 kg/ha N applied to the control and 150 kg/ha applied to the fresh and historic PS treatments	8/4/14
Annual soil sample	28/4/14
35kg/ha K_2O, 50 kg/ha SO_3 & 5 kg/ha $MnSO_4$ to all treatments	6/5/14
Winter wheat harvested	7/8/14

Appendix 3: Storage Study Method Statement

EQual Project (30636) Method Statement:
Storage study

This method statement details the procedures to be followed for the storage study being undertaken at ADAS Gleadthorpe.

In order to determine the effects of storage on the chemical composition of poultry litter ash (PLA) and paper sludge (PS) materials replicated storage heaps will be established at ADAS Gleadthorpe in August 2013 and changes in the composition of the stored materials will be monitored over the course of 12 months. Heaps will be established on a slightly sloping impermeable base in order to collect and analyse any leachate generated from the heaps.

The storage and use of PS must adhere to the requirements of the EA Regulatory Position Statement. The storage and use of PLA must adhere to the PLA Quality Protocol.

Equipment

- Polythene liners, straw bales, drainpipes and tanks to enable leachate collection.
- Portable weigh pads.
- Tinytalk temperature data loggers.
- Litter bags, ties, string and waterproof labels.
- 1kg plastic tubs (supplied by NLS).
- 120g glass jars (supplied by NLS).
- 300g polypropylene sterile jars (supplied by NLS.)
- 1 litre glass jars.
- Bottles for leachate (supplied by NLS).
- Camera.

Heap construction

Six individual temporary storage heaps (3 replicated PLA heaps & 3 replicated PS heaps) will be established in a series of hydrologically isolated sloping concrete bunkers at ADAS Gleadthorpe. Each bunker will be 3.625m x 3.625m in plan, with two courses of concrete blocks around three of the sides (*c*.0.5m high), and the fourth side contained using straw bales lined with a strip of polythene. Leachate will be collected at the lowest corner of each bunker using a short length of perforated plastic drainage pipe to direct leachate into six individual collection tanks.

Approximately 5 tonnes (fresh weight - FW) of PLA and PS material will be weighed into the bays using portable weigh pads. During construction four 'litter' bags, each containing *c.*2kg of the PLA or PS material will be buried at known, separate locations within the heap. Each litter bag will have a string attached to aid retrieval, with the location of each bag identified by markers on the surface of the heap. Additionally a tinytalk temperature data logger will be placed in each heap set to record the heap temperature on an hourly basis.

Photographs will be taken on heap construction and at each sampling occasion. The heaps will be dismantled at the end of the 12 month storage period.

Sampling

Representative samples will be taken for laboratory analysis at NLS and archiving at Gleadthorpe, in accordance with the EA project specification '30636 EQual programme agriculture field trials Jan 2013':

Samples of the material contained within each heap will be taken on construction in August 2013 (3 samples of each material, *c*.2kg per sample). Samples will be split and placed into the appropriate sample bottles, and sent to NLS for analysis.

The litter bags will be removed at 1, 3, 6 and 12 months after heap construction. Samples within the litter bags will be split and placed in the appropriate sample bottles and sent to NLS for analysis.

Samples for e-coli and salmonella analysis should be dispatched to NLS on the same day of sampling. A subsample of each material will also be placed in glass jars for storage in the archive at Gleadthorpe.

Leachate from each heap will be collected in a series of prefabricated, calibrated containers of appropriate size. If leachate arises, the volume collected will be measured at fortnightly/monthly intervals (up to a maximum of 12 sampling dates and therefore 6x12=72 samples over the period September 2013 to August 2014, depending on rainfall). Samples will be taken from the collected bulk of leachate from each heap, will be split and placed into the appropriate sample bottles, and sent to NLS for analysis.

All samples should be stored in a fridge (<4°C) and sent, fresh, in a cool box (with ice packs) via overnight carrier or equivalent. Do not dispatch samples on a Friday, as they may deteriorate over the weekend. Please inform NLS of their dispatch and expected time of arrival. All glass bottles for sample storage should be washed (i.e. in a normal dishwasher using clean water only) before use, to remove any residues.

Labelling

Samples will be labelled with a unique identifier as detailed in Table 1.

Table 1 Sample labelling

Treatment (heap)	Sample type	Reference label[a]
PLA rep 1	PLA material	SSPLAPLA-1 *Sample date*
PLA rep 2	PLA material	SSPLAPLA-2 *Sample date*
PLA rep 3	PLA material	SSPLAPLA-3 *Sample date*
Paper sludge rep 1	PS material	SSPSFPSF-1 *Sample date*
Paper sludge rep 2	PS material	SSPSFPSF-2 *Sample date*
Paper sludge rep 3	PS material	SSPSFPSF-3 *Sample date*
PLA rep 1	Leachate	SSPLALEAC1 *Sample date*
PLA rep 2	Leachate	SSPLALEAC2 *Sample date*
PLA rep 3	Leachate	SSPLALEAC3 *Sample date*
Paper sludge rep 1	Leachate	SSPSFLEAC1 *Sample date*
Paper sludge rep 2	Leachate	SSPSFLEAC2 *Sample date*
Paper sludge rep 3	Leachate	SSPSFLEAC3 *Sample date*

[a]The reference label should be followed by the date of sampling

Roles and Responsibilities

All activities will be conducted by a team led by the Site Manager.

Data Recording

An entry will be made in the experimental diary to record the date and time of heap construction, and all sampling occasions, the weather conditions, sampler name and laboratory dispatch date and details. Heap temperatures at a single point in the 'centre' of each heap will be recorded on a daily basis using temperature logging equipment. Weather variables routinely monitored by the onsite meteorological station at Gleadthorpe will be used to assist in interpretation of results, in particular daily rainfall and ambient air temperatures.

Health and Safety

- Avoid getting the material on the skin, but if this happens wash it off as soon as possible. Wash hands and forearms thoroughly before handling food, drinking or smoking.

- Leptospirosis (Weil's disease), a serious and sometimes fatal infection is transmitted to humans by contact with urine from infected rats. As rats often scavenge organic material stores, take precautions as specified in HSE Agriculture Information Sheet no. 2.

- Handling organic material may expose workers to other serious infectious diseases. These include poliomyelitis, tetanus, typhoid fever, hepatitis A and hepatitis B. See Occupational Health Service Notice 93/6.

- Wear waterproof boots, waterproof jacket, trousers and gauntlets or long gloves, when sampling organic materials. Wear a face shield where splashing of material may occur. Wear a dust mask or preferably an airstream helmet when sampling dusty materials.

- Ensure that the outside of sample bags and containers are clean and free from contamination so that reception staff at the laboratory are not exposed to biohazards.

- The site specific risk assessment at each experimental location (which already considers organic material application and sampling) will be consulted before and after application. If any amendments are required, the risk assessment will be updated.

Appendix 4: Changes in soil properties between Sept 2013 (baseline) and April 2014

Determinand	*Gleadthorpe*					*Harper Adams*				
	Control		*Fresh PS*		*Time P*[1]	*Control*		*Fresh PS*		*Time P*[1]
	Sept 13	*April 14*	*Sept 13*	*April 14*		*Sept 13*	*April 14*	*Sept 13*	*April 14*	
Nitrogen (%)	0.08	0.10	0.08	0.08	*NS*	0.18	0.16	0.19	0.13	***0.004*** ↓
Ammoniacal nitrogen (mg/kg)	<2	<2	<2	<2	*NS*	<3	<2	<2	<2	*NS*
Nitrate nitrogen (mg/kg)	<3	<3	<3	<3	*NS*	12.4	5.34	12.8	5.19	***0.02*** ↓
Total (carbon)	1.00	1.27	1.07	1.40	***0.01*** ↑	1.52	1.59	1.58	1.63	*NS*
C:N	13	16.3	13	18.3	*NS*	8	9.6	8	12.3	***0.006*** ↑
Conductivity (µs/cm)	1997	2120	2010	2203	***0.008*** ↑	2060	2123	2063	2087	***0.002*** ↑
pH	6.7	6.20	6.8	6.54	*NS*	6.8	6.45	6.5	7.01	*NS*
Extractable P (mg/l)	38.8	43.3	41.9	51.1	*NS*	66.7	89.7	100.2	88.8	*NS*
Extractable K (mg/l)	65.8	62.8	77.2	75.8	*NS*	125	119	180	148	*NS*
Extractable Mg (mg/l)	67.3	62.3	42.3	42.8	*NS*	47.3	48.0	45.0	47.5	*NS*
Aluminium (mg/kg)	4707	4453	4997	4940	*NS*	10867	11367	11133	11133	*NS*
Antimony (mg/kg)	<1	<1	<1	1.02	*NS*	<1	1.08	<1	<1	*NS*
Arsenic (mg/kg)	4.33	4.52	4.39	4.41	*NS*	6.32	6.89	6.52	6.75	*NS*
Barium (mg/kg)	23.1	22.1	23.7	23.6	*NS*	61.2	64.2	61.8	61.3	*NS*
Beryllium (mg/kg)	0.31	0.31	0.34	0.35	*NS*	0.51	0.56	0.52	0.54	*NS*
Boron (mg/kg)	2.61	2.64	2.59	3.50	*NS*	7.28	8.70	7.43	7.77	*NS*
Cadmium (mg/kg)	<0.2	<0.2	<0.2	<0.2	*NS*	<0.2	<0.2	<0.2	<0.2	*NS*
Calcium (mg/kg)	1273	1006	1529	1852	*NS*	2533	2610	2483	2483	*NS*
Chromium (mg/kg)	6.55	6.70	6.65	6.73	*NS*	13.8	15.4	14.2	15.4	*NS*
Chromium Hexavalent (mg/kg)	<0.6	<0.6	<0.6	<1.2	*NS*	<0.6	<1.2	<0.6	<0.6	*NS*
Cobalt (mg/kg)	1.74	1.84	1.83	1.78	*NS*	3.90	4.57	4.19	4.11	*NS*
Copper (mg/kg)	4.62	4.27	4.92	5.34	*NS*	13.4	13.2	13.9	13.4	*NS*
Iron (mg/kg)	7743	7040	7487	7117	***0.006*** ↓	11733	12133	11733	11767	*NS*
Lead (mg/kg)	15.5	15.8	15.3	15.0	*NS*	19.4	19.9	18.9	18.2	*NS*
Lithium (mg/kg)	6.00	5.91	6.85	6.62	*NS*	14.3	15.2	15.1	15.0	*NS*
Magnesium (mg/kg)	696	671	809	683	*NS*	2410	2443	2527	2417	*NS*
Manganese (mg/kg)	186	185	155	148	*NS*	277	312	298	284	*NS*
Mercury (mg/kg)	<0.2	<0.2	<0.2	<0.2	*NS*	<0.2	<0.2	<0.2	<0.2	*NS*
Molybdenum (mg/kg)	<1	<1	<1	<1	*NS*	<1	<1	<1	<1	*NS*
Nickel (mg/kg)	3.88	3.97	4.28	4.40	*NS*	10.2	11.4	10.5	11.5	***0.02*** ↑
Phosphorus (mg/kg)	582	514	583	601	*NS*	1107	1167	1203	1147	*NS*
Potassium (mg/kg)	694	656	730	700	*NS*	2207	2263	2357	2283	*NS*
Selenium (mg/kg)	<1	<1	<1	<1	*NS*	<1	<1	<1	<1	*NS*
Silver (mg/kg)	<1	<1	<1	<1	*NS*	<1	<1	<1	<1	*NS*
Sodium (mg/kg)	25.7	23.7	28.2	27.8	*NS*	62.0	62.6	64.3	60.6	*NS*
Strontium (mg/kg)	4.64	4.25	5.46	5.89	*NS*	9.18	9.80	9.30	9.13	*NS*
Thallium (mg/kg)	<1	<1	<1	<1	*NS*	<1	<1	<1	<1	*NS*
Tin (mg/kg)	1.04	<1	1.09	1.04	*NS*	1.34	1.32	1.35	<1	*NS*
Titanium (mg/kg)	74.1	77.6	73.7	75.6	*NS*	107	119	110	116	***0.05*** ↑
Vanadium (mg/kg)	10.2	10.0	10.1	9.94	*NS*	17.7	19.2	18.2	18.4	*NS*
Zinc (mg/kg)	25.9	25.0	25.5	27.5	*NS*	63.4	65.3	64.2	63.0	*NS*
E-coli (No/g)	<9	<1	<9	<1	*NS*	<10	<1	<9	<1	*NS*
Biomass C (mg/kg)	81	55	70	39	***0.002*** ↓*	157	179	158	153	*NS*
Biomass N (mg/kg)	16	18	14	14	***0.02*** ↓*	25	26	26	30	***0.003*** ↑*
Aggregate stability (%)	10	16	10	16	*NS*	*6.2*	7	6.9	7	*NS*

[1]Statistical analysis undertaken by analysis of variance, with time and treatment as factors; NS = not significant (*P*>0.05); ↑↓Direction of change (increase or decrease over time); * indicates a significant interaction between

Appendix 5: Effect of repeated PS additions on topsoil properties.

Effect of historic repeated PS additions on topsoil chemical parameters, January 2013 (treatment means)

Determinand	*Unit*	*Gleadthorpe*			*Harper Adams*		
		Con	*Historic PS*	*P*	*Con*	*Historic PS*	*P*
Nitrogen	% dm	0.07	0.07	*NS* (0.79)	0.12	0.14	*NS* (0.40)
Ammoniacal nitrogen	mg/kg dm	<0.2	<0.2	-	11.7	1.0	*NS* (0.11)
Nitrate nitrogen	mg/kg dm	7.11	6.76	*NS* (0.87)	42.4	19.7	**0.05**
Total carbon	% dm	1.05	1.46	*NS* (0.08)	1.34	1.67	**0.04**
Organic matter	% dm	2.03	2.23	*NS* (0.72)	2.75	3.17	**0.04**
C:N ratio	ratio	15	20	*NS* (0.07)	11	12	**0.02**
Dry matter	%	88.9	87.6	*NS* (0.14)	93.9	88.4	*NS* (0.06)
Conductivity	µs/cm	2093	2003	**0.004**	2120	2067	**0.03**
pH	unit	5.69	7.92	**<0.001**	6.11	7.89	**0.005**
Extractable P	mg/l	53.6	47.2	*NS* (0.60)	79.4[1]	73.2	*NS* (0.57)
Extractable K	mg/l	68.7	65.4	*NS* (0.72)	162	144	*NS* (0.50)
Extractable Mg	mg/l	67.8	20.3	**<0.001**	57.1	31.7	**0.006**
Aluminium	mg/kg dm	5337	5683	*NS* (0.67)	11333	11900	*NS* (0.48)
Antimony	mg/kg dm	<10.0	<10.0	-	<10.0	<10.0	-
Arsenic	mg/kg dm	4.90	4.18	*NS* (0.17)	6.19	6.24	*NS* (0.92)
Barium	mg/kg dm	30.7	30.5	*NS* (0.93)	64.3	67.7	*NS* (0.60)
Beryllium	mg/kg dm	0.34	0.31	*NS* (0.41)	0.47	0.47	*NS* (0.96)
Boron	mg/kg dm	3.60	5.33	*NS* (0.08)	8.45	8.33	*NS* (0.71)
Cadmium	mg/kg dm	<0.25	<0.25	-	<0.25	<0.25	-
Calcium	mg/kg dm	908	7427	**0.03**	2237	14067	**0.02**
Chromium	mg/kg dm	7.25	7.08	*NS* (0.88)	13.4	13.7	*NS* (0.81)
Chromium Hexavalent	mg/kg dm	<0.30	<0.30	-	<0.30	<0.30	-
Cobalt	mg/kg dm	1.97	1.82	*NS* (0.48)	3.79	4.82	*NS* (0.45)
Copper	mg/kg dm	5.56	6.06	*NS* (0.52)	12.5	14.5	*NS* (0.13)
Iron	mg/kg dm	8407	7730	*NS* (0.47)	11267	11533	*NS* (0.82)
Lead	mg/kg dm	16.5	14.9	*NS* (0.31)	17.4	17.0	*NS* (0.73)
Lithium	mg/kg dm	5.96	7.32	*NS* (0.46)	14.7	16.0	*NS* (0.49)
Magnesium	mg/kg dm	783	752	*NS* (0.71)	2393	2550	*NS* (0.56)
Manganese	mg/kg dm	204	182	*NS* (0.47)	281	327	*NS* (0.56)
Mercury	mg/kg dm	< 2.00	< 2.00	-	< 2.00	< 2.00	-
Molybdenum	mg/kg dm	< 2.00	< 2.00	-	< 2.00	< 2.00	-
Nickel	mg/kg dm	4.33	4.22	*NS* (0.83)	9.85	10.2	*NS* (0.76)
Phosphorus	mg/kg dm	659	680	*NS* (0.88)	1060	1183	*NS* (0.37)
Potassium	mg/kg dm	704	735	*NS* (0.75)	2137	2160	*NS* (0.84)
Selenium	mg/kg dm	<1.00	<1.00	-	<1.00	<1.00	-
Silver	mg/kg dm	<10.0	<10.0	-	<10.0	<10.0	-
Sodium	mg/kg dm	29.4	37.2	*NS* (0.07)	62.0	71.5	*NS* (0.16)
Strontium	mg/kg dm	2.67	16.4	**0.02**	8.33	28.0	**0.03**
Thallium	mg/kg dm	<3.00	<3.00	-	<3.00	<3.00	-
Tin	mg/kg dm	<20.0	<20.0	-	<20.0	<20.0	-
Titanium	mg/kg dm	68.0	67.0	*NS* (0.92)	92.5	96.5	*NS* (0.69)
Vanadium	mg/kg dm	11.0	10.0	*NS* (0.48)	17.2	17.3	*NS* (0.95)
Zinc	mg/kg dm	29.8	32.2	*NS* (0.66)	60.3	68.6	*NS* (0.21)

[1] Mean of two replicate plots

Statistical analysis undertaken by t-test; NS = not significant (*P*>0.05)

Effect of historic repeated PS additions on topsoil biomass and aggregate stability, January 2013 (treatment means with standard errors in parenthesis; n=3)

Treatment	Biomass C (mg/kg soil)		Biomass N (mg/kg soil)		Aggregate stability (% w/w)[3]	
Site[1]	GT	HA	GT	HA	GT	HA
Control	69 (6.3)[a]	168 (1.2)[a]	14 (1.0)[a]	31 (2.0)[a]	14 (1.2)	8 (2.1)
Historic PS	119 (19.1)[b]	235 (18)[b]	30 (1.72)[b]	47 (4.1)[b]	15 (1.5)	9 (1.1)
P[2]	*NS* (0.07)	*NS* (0.07)	**0.001**	**0.027**	*NS* (0.63)	*NS* (0.68)

[1]GT: Gleadthorpe; HA: Harper Adams

[2]Statistical analysis undertaken by t-test; NS=not significant (*P*>0.05)

[3]Aggregate stability measured by the dispersion ratio (ratio of silt and clay suspended by mild slaking forces expressed as a % of the total silt and clay content); Ratios in the range 6-10% suggest the soil is 'stable', 11-15% indicate that the soil is 'fairly stable', while ratios in the range 16-25% suggest the soil is 'somewhat unstable' (Anon, 1982).