Assessing the effectiveness of a three-stage on-farm biobed in treating pesticide contaminated wastewater

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11 Abstract

Agricultural point source pesticide pollution arising from contaminated machinery washings and 12 accidental spillages pose a significant threat to river water and groundwater quality. In this study, we 13 14 assess the effectiveness of a three-stage on-farm biobed for treating pesticide contaminated waste water from a large (20 km²) commercial arable estate. The facility consisted of an enclosed 15 machinery wash-down unit (stage 1), a 49 m² lined compost-straw-topsoil biobed (stage 2), and a 16 200 m² drainage field with a trickle irrigation system (stage 3). Pesticide concentrations were 17 18 analysed in water samples collected fortnightly between November 2013 and November 2015 from 19 the biobed input and output sumps and from 20 porous pots buried at 45 cm and 90 cm depth 20 within the drainage field. The results revealed that the biobed removed 68-98% of individual 21 pesticides within the contaminated washings, with mean total pesticide concentrations reducing by 22 91.6% between the biobed input and output sumps. Drainage field irrigation removed a further 68-23 99% of individual pesticides, with total mean pesticide concentrations reducing by 98.4% and 97.2% 24 in the 45 cm and 90 cm depth porous pots, respectively. The average total pesticide concentration at 45 cm depth in the drainage field (57 μ g L⁻¹) was 760 times lower than the mean concentration 25 recorded in the input sump (43,334 μ g L⁻¹). There was no evidence of seasonality in the efficiency of 26 27 biobed pesticide removal, nor was there evidence of a decline in removal efficiency over the twoyear monitoring period. However, higher mean total pesticide concentrations at 90 cm (102 µg L⁻¹) 28 relative to 45 cm (57 μ g L⁻¹) depth indicated an accumulation of pesticide residues deeper within the 29 30 soil profile. Overall, the results presented here demonstrate that a three-stage biobed can 31 successfully reduce pesticide pollution risk from contaminated machinery washings on a commercial 32 farm.

33 **Keywords:** Biobed; pesticide; herbicide; biodegradation; water quality; arable

34 **1. Introduction**

35 The widespread use of pesticides in agriculture to kill plant and insect pests which would otherwise 36 reduce crop yields has been instrumental in enhancing global agricultural productivity since the mid-37 20th century (Oerke and Dehne, 2004; Oerke, 2005; Clarke et al., 2011; Popp et al., 2013). However, the harmful environmental impacts of applying toxic chemicals across large areas of the planet's 38 39 surface, particularly on the aquatic environment, are coming under increasing scrutiny (Skinner et 40 al., 1997; DeLorenzo et al., 2001; Schwarzenbach et al., 2010). High profile cases, such as the effect 41 of the insecticide DDT on the hatching success of raptors in the 1960s and 1970s, brought into focus 42 the potential for pesticides to bio-accumulate through the food chain and negatively impact upon 43 non-target species (Ames, 1966; Connell, 1988; Arnot and Gobas, 2006). Similarly, recent research 44 has linked the use of neonicotinoid insecticides to the decline of bee populations in Europe and 45 North America (Blacquiere et al., 2012; Whitehorn et al., 2012). Studies have also highlighted the significant economic costs associated with removing pesticides from drinking water. Between 1991 46 47 and 2000, water companies in the United Kingdom spent £2 billion treating pesticide contaminated water supplies (Jess et al., 2014), whilst in the United States the deleterious impacts of pesticide use 48 49 were estimated to cost \$9.6 billion in 2005 alone (Pimentel, 2005).

50 In order to tackle pesticide pollution, a range of national and international legislation is currently in 51 force. Under the EU Water Framework Directive (2000/60/EC), specifically the Drinking Water 52 (98/83/EC) and Groundwater (2006/118/EC) Directives, European Union member states must ensure that no individual pesticide concentration in drinking water at the tap exceeds 0.1 µg L⁻¹ and total 53 pesticide concentrations should not exceed 0.5 µg L⁻¹. Additionally, the Pesticides Framework 54 55 Directive (2009/128/EC) aims to reduce the damage caused by pesticides through the adoption of sustainable usage practices. In the United States, similar legislation exists under the Safe Drinking 56 57 Water Act (1974) which places individual concentration limits on specific pesticides.

Pesticide pollution can either arise from diffuse sources, such as spray drift, leaching and overland flow, or from point sources, such as accidental spillages, leakages from equipment or from contaminated machinery washings (Carter, 2000; De Wilde et al., 2007). Whilst diffuse sources can in part be reduced by behavioural changes, such as timing of spraying to avoid periods of wet and windy weather to limit pesticide mobility, biobeds have emerged as a potentially important

mitigation strategy for dealing with point source pollution (Fogg et al., 2003a; Reichenberger et al.,
2007; Karanasios et al., 2010; Omirou et al., 2012).

65 The biobed concept originated in Sweden in the 1990s as a way of using microbial activity to degrade 66 waste pesticide residues (Torstensson, 2000). A biobed is essentially a moderately sized pit (typically 67 tens of cubic metres in volume) which can be lined or unlined and is filled with a 1:2:1 matrix of 68 compost, straw and topsoil. The surface is covered with grass and onto this the waste pesticide 69 residues are deposited. In principle, microorganisms (e.g. bacteria and fungi) within the biobed 70 matrix chemically and physically interact with the pesticides leading to structural changes and/or 71 complete degradation (Pinto et al., 2016). To work effectively, the biobed mixture needs to have 72 high pesticide absorption capacity and be able to facilitate high rates of microbial activity (Castillo et 73 al., 2008). For this reason, straw is included to enhance microbial activity, particularly that of lignin-74 degrading fungi (e.g. white rot fungi) which produce phenoloxidase enzymes that have a broad 75 specificity and are thereby able to degrade a wide range of pesticide residues (Bending et al., 2002). 76 Soil is included to increase the sorption capacity of the matrix material so that it holds onto the 77 pesticides and also provides a source of microorganisms for biodegradation. Lastly, compost is 78 added to increase sorption capacity, improve moisture content and decrease the pH to make 79 conditions favourable for fungi growth. The surface grass layer aids water regulation and prevents 80 surface crusting, thus limiting the formation of cracks that would open up preferential pathways for 81 pesticides to escape the biobed prior to degradation (Fogg et al., 2004; Castillo and Torstensson, 82 2007; Castillo et al., 2008). In lined biobed systems, common in the United Kingdom (UK), the leachate is typically collected from the bottom of the biobed and re-used for either irrigation, 83 84 sprayer washing or as a carrier for further herbicide applications. Irrigation can be on infield crops or 85 a designated drainage area. In order to minimise pollution risk and comply with UK environmental 86 protection legislation, the drainage area must be vegetated, be neither frozen or water logged, 87 be >10 m away from any surface waterbody, be >50 m from any spring, well or borehole not used for domestic supply or food production, and be >250 m away from any borehole that is used for 88 89 domestic supply or food production (Environment Agency, 2007).

Established in 2010, the River Wensum Demonstration Test Catchment (DTC) project is a part of a UK government funded initiative to evaluate the extent to which on-farm mitigation measures can be employed to cost effectively reduce the impacts of agricultural pollution on river ecology whilst maintaining food production capacity (Outram et al., 2014). Draining a catchment area of 660 km² in Norfolk, UK, of which ~63% is arable land, the River Wensum supplies drinking water for the city of Norwich and is affected by agricultural pesticide pollution. A small unpublished water quality

96 monitoring study carried out at 20 locations on the River Wensum over a 16-week period in autumn 97 2012, revealed that 23% of samples contained individual pesticide concentrations greater than the 0.1 µg L⁻¹ drinking water limit. Five key pesticides (metaldehyde, metazachlor, dimethenamid, 98 99 flufenacet and propyzamide) accounted for 90% of all detected compounds, with 21% of samples containing metaldehyde concentrations >1 μ g L⁻¹ (further details of this study can be found in the 100 101 electronic supplementary material). Partly in response to this pesticide pollution pressure, an on-102 farm biobed unit capable of treating contaminated machinery washings was installed at Manor 103 Farm, Salle, in the Blackwater sub-catchment of the River Wensum. This was part of a trial package 104 of on-farm mitigation measures, co-funded under the Catchment Sensitive Farming (CSF) initiative 105 (Natural England, 2014), aimed at reducing agricultural pollution.

- 106 The primary objectives of this paper are as follows:
- 107 (i) To assess the efficiency of the Manor Farm biobed at reducing pesticide concentrations in
 agricultural machinery washings;
- 109 (ii) To assess the effectiveness of drainage field irrigation at further reducing pesticide110 concentrations in biobed leachate;
- 111 (iii) To determine if biobed pesticide removal is more efficient for certain types of pesticide;
- 112 (iv) To assess temporal variability in the effectiveness of the biobed.
- 113

114 **2. Methods**

115 2.1 Study Location

This study focuses upon a biobed unit installed in 2013 at Manor Farm, Salle Park Estate, Norfolk, UK 116 (52°46'57"N, 01°08'07"E). The large, commercial Salle Park Estate covers 20 km² of which 79% is 117 118 intensive arable land managed with a seven-year crop rotation of winter wheat, winter and spring 119 barley, winter oilseed rape, spring beans and sugar beet. The estate also comprises 15% improved 120 grassland, 5% mixed woodland and 1% rural settlements. Across the estate, 16,387 litres of 121 concentrated liquid pesticide and 1,230 kg of solid pesticide granules were applied in 2014, the 122 majority of which was applied during spring (March – May). Prior to the installation of the biobed, 123 the risk of pesticide pollution occurring was relatively high. Farm machinery was washed down in the 124 farmyard on concrete hard standing and the wastewater was collected in a drain with an isolation

- valve from where it was subsequently transported to a designated disposal area 0.8 km from the
 farm. However, the drain isolation valve was manually operated and human error could result in the
- 127 contaminated washings discharging directly into a nearby pond.
- 128

129 2.2 Biobed Facility

- 130 The Manor Farm biobed facility consists of three main components (Figures 1 and 2):
- (i) Wash-down unit: a 20 m x 9 m enclosed concrete wash-down unit is used to both
 remove pesticides residues from farm machinery and to contain any pesticides spilt
 during the filling of the pesticide sprayer. A drain running down the centre of the unit
 channels contaminated washings into a concrete storage tank (the input sump);
- **Biobed**: the biobed itself is an uncovered, indirect, lined (impermeable geomembrane)
 design covering an area of 49 m² (7 m x 7 m) to a depth of 1.2 m, thus providing a large
 surface area for biological and photo-degradation The organic bio-mix matrix material is
 composed of a 1:2:1 mix of peat-free compost, chopped wheat/barley straw and local
 topsoil. The surface is seeded with grass. Contaminated water from the input sump is
 pumped onto the biobed surface via a trickle irrigation system, with the leachate
 collected at the base of the biobed in a concrete output sump;
- **Drainage field**: the leachate from the output sump is pumped onto a 200 m² (20 m x 10 142 (iii) 143 m) drainage field via a second trickle irrigation system buried just below the surface to 144 promote further removal of residual pesticide residues. This drainage field is covered 145 with grass and is surrounded by seven mature trees. A network of 20 porous pots were 146 installed (30° angle) across the drainage area at 45 cm and 90 cm depth (ten pots for 147 each) to monitor soil water pesticide concentrations at depth for signs of further removal or accumulation. As far as the authors are aware, this is the first time that 148 149 pesticide removal in a drainage field on a commercial farm has been routinely 150 monitored.
- The biobed is designed to treat >15,000 L of contaminated wastewater from the wash-down unit per year. The trickle irrigation pumps are controlled by float-switches within the input and output sumps so that irrigation commences automatically once the water depth within the sumps has reached a predefined level. During the winter, the irrigation systems are switched off to prevent ice damage.
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157 2.3 Sample Collection

158 Water samples were collected from the input and output sumps and the 45 cm and 90 cm porous 159 pots at approximately two week intervals between November 2013 and November 2015. No 160 sampling took place between June 2014 and November 2014 due to a hiatus in funding. On each 161 sampling occasion eight water samples were collected to enable a range of analyses – three from each of the input and output sumps and one each from the 45 cm and 90 cm porous pots. Water 162 163 from the sumps was collected using a stainless steel bucket lowered into the chambers on a chain and was decanted into a 1 L glass bottle (sample code = PESTP) and two 250 mL polyethylene 164 165 terephthalate (PET) bottles for each sump. To preserve the samples, one PET bottle had 2 mL of 3 166 molar formic acid added (HERBP), whilst the other contained 2 mL of 2.65 molar formic acid and 5 167 molar ammonium acetate (URON). For the drainage field, each 45 cm and 90 cm porous pot was put 168 under vacuum for 20 minutes to extract soil water. Recovered soil water was bulked together to 169 produce a single sample for each depth and was decanted into a 250 mL PET bottle containing 2 mL 170 of 3 molar formic acid preservative (HERBP). The volume of soil water collected varied seasonally 171 depending on soil moisture conditions, with up to 200 mL collect during the winter and <50 mL 172 collected during the summer. Throughout summer and autumn 2015, dry soil conditions meant no 173 samples could be collected from the 45 cm porous pots. Note that in any given week, samples 174 collected from the input sump, output sump and the drainage field did not correspond to the same 175 body of contaminated water. Instead, samples collected from the drainage field corresponded to 176 water that was in the output sump several days/weeks prior to sampling.

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178 2.4 Sample Analysis

All samples were analysed by the Environment Agency's National Laboratory Service. Three differentanalytical techniques were employed to determine a wide variety of pesticide compounds:

(i) Phenoxy acidic herbicides (HERBP): a 1000 μL aliquot was transferred into a silanised vial
 and an internal standard was added. 400 μL of the sample was then injected into a high
 performance liquid chromatograph (HPLC) interfaced to a triple quadrupole mass
 spectrometer (TQMS) operated in positive and negative atmospheric pressure electrospray

mode. Tandem mass spectroscopy data (MS/MS) were acquired in multiple reaction
monitoring mode;

- 187 (ii) Phenyl urea herbicides, *n*-methyl carbamates, fungicides and asulam (URON): a 1000 μ L 188 aliquot was transferred into a silanised vial and ethylenediaminetetraacetic acid (EDTA) and 189 an internal standard were added. A 100 μ L sample was then injected into the HPLC and 190 analysed as for HERBP;
- (iii) Triazines, organophosphorus and miscellaneous pesticides (PESTP): pesticides were
 extracted into dichloromethane using liquid-liquid extraction. The extract was then
 concentrated and injected into a gas chromatograph interfaced with a mass spectrometer
 (GC-MS) operating in electron ionisation mode. The collected results were then compared
 with data obtained from a series of similarly treated standard solutions in data handling
 software;

197 In total, 86 pesticides were detected and here we primarily focus on 15 compounds which were 198 regularly used, had high input concentrations (>100 μ g L⁻¹) and/or are CSF key indicator pesticides. 199 The physico-chemical properties of these pesticides, which are all herbicides and which accounted 100 for ~98.6% of all compounds measured in the input sump, are presented in Table 1. Insufficient 101 water was collected from the drainage field to enable the full suite of analyses to be carried out and 102 therefore the porous pot analysis was restricted to a smaller number of compounds (HERBP only).

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204 **3. Results**

205 **3.1 Total Pesticide Concentration**

206 The total concentrations for all 86 pesticides measured at the four monitoring points between 207 November 2013 and November 2015 are shown in Figure 3. Mean pesticide concentrations over this period were: 43,334 μ g L⁻¹ (range = 1037–508,873 μ g L⁻¹) in the input sump; 3647 μ g L⁻¹ (47–42,260 208 μ g L⁻¹) in the output sump; 57 μ g L⁻¹ (0.5–192 μ g L⁻¹) in the 45 cm depth porous pots; and 102 μ g L⁻¹ 209 210 $(2-396 \ \mu g \ L^{-1})$ in the 90 cm depth porous pots. Overall, this corresponds to a 91.6% reduction in 211 pesticide concentration between the biobed input and output sumps, with a further 98.4% and 212 97.2% reduction between the output sump and the 45 cm and 90 cm drainage field porous pots, 213 respectively. Substantial temporal variability in the input sump concentrations reflect both variations 214 in the amount of pesticide being applied across the farm at any one time and in the amount of water used during the washing of farm machinery (i.e. lower pesticide concentrations result when more water is used). Similarly, fluctuations in the output sump and porous pot concentrations will also reflect variability in precipitation which has the potential to both dilute and flush out pesticide residues within the biobed and drainage field.

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220 3.2 Individual Pesticide Concentrations

Individual pesticide concentration data for the 15 key pesticides are presented in Table 2. The 221 highest mean pesticide concentration recorded in the input sump (26,935 μ g L⁻¹) was for 222 ethofumesate, a widely applied herbicide to kill grass and broadleaf weeds in sugar beet crops. 223 224 The lowest mean concentration (15.3 µg L⁻¹) recorded was for carbetamide, a grass/broadleaf herbicide applied to oilseed rape. The efficiency of individual pesticide reduction between the 225 226 input and output sumps ranged from 97.6% for propyzamide to 68.4% for metazachlor, with 227 seven out of 15 pesticides achieving >90% reduction in mean concentration. Mean concentrations in the 45 cm depth drainage field porous pots varied between 1.1 μ g L⁻¹ for bromoxynil and 228 MCPA, to 9.3 µg L⁻¹ for fluroxypyr. Similarly, in the 90 cm porous pots, bromoxynil and MCPA had 229 the lowest mean concentrations (1.6 μ g L⁻¹), whilst clopyralid had the highest concentration (16.2 230 231 $\mu g L^{-1}$). The efficiency of pesticide removal between the output sump and the 45 cm porous pots 232 ranged from 99.0% for 2,4-D to 77.1% for MCPA, whilst in the 90 cm porous pots efficiencies 233 ranged from 97.0% for 2,4-D to 68.3% for dicamba.

234

235 4. Discussion

236 4.1 Biobed Efficiency

237 The biobed proved to be highly effective in reducing the concentrations of pesticide within the 238 contaminated machinery washings, lowering total pesticide concentrations by an average of 91.6%. 239 This compares with pesticide removal efficiencies of 52-100% recorded for a wide range of 240 chemicals in other biobed studies conducted across Europe (De Wilde et al., 2007). Nevertheless, the mean total pesticide concentration (3647 μ g L⁻¹) and the mean concentrations of individual 241 pesticides (3-1755 µg L⁻¹) within the output sump remained sufficiently large to pose an 242 243 environmental risk. These output concentrations are consistent with the results of similar studies 244 assessing biobed removal efficiencies (e.g. Spliid et al., 2006). Irrigation of the biobed leachate in the

drainage field was therefore necessary for promoting further pesticide removal. In the top 45 cm of the soil, total pesticide concentrations were reduced by 98.4% to 57 μ g L⁻¹, whilst individual pesticide concentrations were reduced by 77.1–99.0% to 1.1–9.3 μ g L⁻¹. These results clearly demonstrate that collecting the leachate from the biobed output sump and applying it onto a drainage field to allow further pesticide removal within the soil profile is essential to reduce concentrations down to more environmentally acceptable levels and represents a significant reduction in risk over the previous farm practice described in Section 2.1.

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253 4.2 Individual Pesticide Removal

254 With the mean pesticide removal efficiency varying by 29.2% between the best (propyzamide) and worst (metazachlor) performing herbicide, it is apparent that the degree of removal achieved is 255 256 dependent upon the chemical structure of the pesticides used. The environmental mobility and 257 persistence of any given pesticide is primarily controlled by its soil sorption characteristics, water 258 solubility and half-life (Arias-Estévez et al., 2008). Highly soluble pesticides with low sorption 259 capacity will tend to move more quickly through the biobed matrix than pesticides with high 260 sorption capacity, and this reduced residence time will diminish the opportunities for microorganisms to degrade these chemicals (i.e. bioavailability will be reduced) (Spliid et al., 2006; 261 De Wilde et al., 2007). Furthermore, most pesticides are degraded by co-metabolic processes. By 262 metabolising constituents within the biobed (e.g. straw), bacteria and fungi produce enzymes which 263 are able to break down toxic chemicals that they otherwise would not be able to degrade (Castillo 264 265 and Torstensson, 2007). However, different pesticide chemical structures have different 266 susceptibility to the oxidative enzymes produced by bacteria and fungi (Ferris and Lichtenstein, 267 1980), and therefore even pesticides with a high sorption capacity that are retained within the 268 biobed may experience low degradation rates.

269 Evidence of these processes can be seen in Figure 4, which shows the relationships between biobed 270 removal efficiency and the typical soil sorption (K_{oc}), water solubility and half-life (DT₅₀) values of the 271 15 pesticides monitored here (data from Lewis et al. (2016)). Despite considerable scatter, there is a positive linear relationship ($R^2 = 0.19$, p = 0.10) between soil sorption and removal efficiency, with 272 five out of six pesticides with the highest sorption coefficients (K_{oc} >100) having high removal 273 efficiencies (>93%). Similarly, there is a significant negative relationship ($R^2 = 0.28$, p = 0.04) 274 between pesticide solubility and removal efficiency, with the six least soluble (<440 mg L^{-1}) 275 pesticides exhibiting the highest levels of removal (>93%). A significant positive relationship (R^2 = 276

277 0.34, p = 0.02) is also apparent between removal efficiency and pesticide half-life, indicating that 278 more persistent pesticides were removed from the leachate more readily than less persistent 279 compounds. However, pesticide sorption coefficients are strongly and significantly correlated with 280 both solubility (r = -0.79, p < 0.01) and DT₅₀ (r = 0.50, p < 0.05) and this in part helps to explain the 281 positive and negative relationships observed between removal efficiency and DT₅₀ and solubility, 282 respectively. In general, pesticides with higher soil sorption coefficients, lower solubility and longer 283 half-lives experienced the greatest removal rates within the Manor Farm biobed.

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285 4.3 Pesticide Accumulation

286 Although total pesticide concentrations were reduced by 98.4% between the output sump and the 287 45 cm porous pots, the mean total pesticide concentration in the 90 cm drainage field porous pots (102 μ g L⁻¹) was nearly double that recorded at 45 cm depth (57 μ g L⁻¹) (Figure 3). Similarly, all 288 289 individual pesticide concentrations were higher at 90 cm depth compared with 45 cm (Table 2), 290 indicating an accumulation of pesticides residues at depth within the drainage field. A potential 291 explanation for this observation comes from examining 1 m depth soil cores taken from the drainage 292 field during porous pot installation which revealed that a silty clay layer dominates the upper 0.5 m 293 whereas sandier material dominates at 0.5–1.0 m depth (Lewis, 2011; Figure SM2 in supplementary 294 material). The clay-rich surface layer would be expected to favour greater pesticide attenuation via 295 sorption onto soil, thus lowering pesticide concentrations in the pore water extracted for analysis. 296 Conversely, the sandier layer at depth would be expected to have lower sorption capacity, thus 297 leaving higher pesticide concentrations in the pore water collected in the porous pots. Additionally, 298 desiccation and fissuring of the surface clay-rich layer could form preferential flow paths deeper into the soil profile, potentially allowing the pesticide leachate to bypass the aerobic surface layers 299 300 where most biological degradation occurs. Ultimately, these processes could result in the drainage 301 field itself acting as a point source of pesticide pollution, particularly if interactions with 302 groundwater increase the lateral mobility of the pesticide residues. These findings emphasise the 303 importance of drainage field design and siting in maximising the removal of pesticides and 304 minimising potential off-site transport.

305

306 4.4 Temporal Trends

307 Successful removal of pesticides within a biobed is dependent upon the biobed matrix supporting a 308 high level of microbial activity and, as such, temperature and moisture content are important factors 309 in determining biobed efficiency. A study by Castillo and Torstensson (2007) demonstrated higher 310 rates of pesticide dissipation when the biobed temperature was at 20° C (compared to 5° C and 10° C) 311 and moisture levels were at 60% (compared to 30% or 90%) of the water holding capacity. 312 Therefore, it might be expected that greater pesticide removal will occur during the summer when 313 temperatures are higher, provided the biobed matrix maintains high moisture content. However, 314 there was no clear evidence of such a trend with the Manor Farm biobed (Figure 3), suggesting that 315 temperature and moisture content may be secondary factors in determining the performance of 316 operational biobeds when compared with laboratory studies. Mean pesticide removal efficiencies 317 between the input and output sumps were 94.5% during the winter (DJF), 97.5% during the spring 318 (MAM) and 92.5% during the summer (JJA). Only autumn (SON), with an efficiency of 75.1%, had 319 significantly lower pesticide removal. This was predominantly due to the very high concentrations of metazachlor recorded in the input (up to 73,900 μ g L⁻¹) and output (up to 27,900 μ g L⁻¹) sumps 320 321 during September – October 2015 after spraying of the autumn sown oilseed rape crop. Prior to 322 autumn 2015, concentrations of metazachlor in the input sump were relatively low (mean = $192 \mu g$ 323 L^{-1}) and the efficiency of biobed removal was high (mean = 94.9%). However, the removal efficiency 324 declined sharply in autumn 2015 (mean = 63.4%), indicating that the biobed was unable to cope with 325 very high metazachlor loading. Although none of the other 14 pesticides analysed here 326 demonstrated this behaviour, similar declines in removal efficiency due to high pesticide loadings 327 have previously been reported in other biobed studies (Fogg et al., 2003b; Vischetti et al., 2008). The 328 effect of poor metazachlor removal in autumn 2015 reduced the overall biobed total pesticide 329 removal efficiency by 2.8%, from 94.4% to 91.6%.

In the UK, it is suggested that the entire biobed matrix is replaced every five years since decomposition of organic matter gradually reduces the efficiency of pesticide removal (Castillo et al., 2008). Over the two-year monitoring period of this study, there was no evidence of a reduction in the biobed performance, with mean biobed removal efficiencies of 91.1% prior to July 2014 and 91.6% after December 2014.

335

336 4.5 Biobed Maintenance

The biobed facility required limited maintenance following its construction in 2013. The biobed matrix was topped up with fresh material in July 2015 after two years of operation as decomposition

339 of organic material had reduced the depth of the bio-mix. At the same time, some re-profiling of the 340 biobed surface was carried out to address slumping in one corner which was causing minor runoff away from the biobed onto the adjacent grassed area. Previous research by Fogg et al. (2004) found 341 342 that uncovered lined biobeds treating large volumes of machinery washings, such as this one here, can become waterlogged without some form of water management, thus resulting in reduced 343 344 microbial activity and lower rates of pesticide degradation. Some evidence of water accumulation on the surface of the Manor Farm biobed was observed during very heavy rainfall events, although such 345 346 incidences were infrequent and of short duration. There was no evidence of reduced biobed 347 performance during the winter when the matrix moisture content would be at its highest level. This 348 confirms that the biobed design was appropriate for handling machinery washings from the Salle 349 Park Estate.

350

351 **4.6 Implications and Economics**

352 The results presented here clearly demonstrate the effectiveness of a straw-compost-topsoil biobed 353 at reducing pesticide residues in substantial volumes of contaminated water generated from machinery washings on a large, arable farm. It is also clear that further treatment of the biobed 354 355 leachate by irrigating the contaminated water through the soil profile of a substantially sized 356 drainage field is beneficial to further reduce pesticide concentrations down to environmentally 357 acceptable levels. Furthermore, the enclosed sprayer wash-down area provides a secure environment when handling pesticide concentrate during sprayer filling operations, thus minimising 358 359 the risk of accidental spillage leading to surface water contamination. Wider scale adoption of 360 biobeds as an on-farm mitigation measure could therefore result in a significant reduction in point 361 source pesticide pollution of streams and rivers draining agricultural catchments. Biobeds are 362 effective in reducing the risks associated with farm pesticide spraying operations since they contain 363 and breakdown pesticides in effluent that could otherwise escape the farm via drainage water. 364 Hence, biobeds are an efficient pesticide reduction measure and are an important tool used by 365 catchment level pollution reduction schemes such as Catchment Sensitive Farming (Environment 366 Agency, 2014; Natural England, 2014). The farmers of the Salle Park Estate also reported that the 367 three-stage biobed significantly improved the efficiency of pesticide handling operations, with 368 pesticide dispensing, machinery washing and wastewater disposal now occurring at a single, purpose 369 built facility.

Table 3 lists the approximate construction costs for the three main components of the Manor Farm
biobed. Whilst total costs were £96,827, the majority of this (£90,454) was for building the large,

372 insulated, wash-down unit and equipping it with mains electricity and steam cleaning equipment. 373 Such a high quality design is not essential to achieve good operational performance and much 374 simpler facilities would be more appropriate for wider deployment across multiple farms within a 375 catchment. The cost of the biobed itself, which included the pipework, pumps, liner, matrix material 376 and labour, was relatively inexpensive (£4311). Replenishment of the matrix material two years after 377 construction cost $\pm 8 \text{ m}^{-2}$. The cost of the drainage field infrastructure was approximately ± 1684 , of 378 which the porous pots accounted for £1466. Installing porous pots in other commercial biobeds 379 would not be necessary as their installation here was purely for research purposes. Much simpler 380 designs could likely be constructed for £5000–10,000, increasing the feasibility of uptake by a larger 381 number of farms, particularly if such measures were financially incentivised under government agri-382 environment schemes.

383

384 **5. Conclusion**

385 Pesticide pollution threatens the sustainable ecosystem functioning of rivers draining agricultural 386 catchments and therefore mitigation measures are required to reduce the amount of pesticides entering freshwater environments. In this study, we have demonstrated how an on-farm biobed is 387 388 capable of reducing the risk of point source pesticide pollution by substantially decreasing pesticide concentrations in large volumes of contaminated machinery washings from a 20 km² arable estate. 389 The three-stage biobed facility, consisting of an enclosed machinery wash-down unit, a 49 m² lined 390 compost-straw-topsoil biobed and a 200 m² drainage field, provided an efficient and secure 391 392 environment for pesticide handling and mixing operations, containing contaminated washings and 393 removing waste pesticide residues. Water quality monitoring over a two-year period revealed 394 individual pesticide concentrations reduced by 68-98% between the biobed input and output 395 sumps, with mean total pesticide concentrations reducing by 91.6%. Further treatment of the 396 contaminated washings in the drainage field removed an additional 68-99% of individual residual 397 pesticides, with total mean pesticide concentrations reducing by a further 98.4% and 97.2% in the 45 398 cm and 90 cm depth porous pots, respectively. Mean total pesticide concentrations at 45 cm depth $(57 \ \mu g \ L^{-1})$ after drainage field irrigation were 760 times lower than that recorded in the untreated 399 machinery washings (43,334 μ g L⁻¹). Although the treated effluent still requires careful handling to 400 401 avoid contaminating freshwater bodies, this nevertheless represents a substantial reduction in 402 groundwater pesticide pollution risk compared with the previous farm practice of disposing of 403 untreated waste washings in a designated disposal area. The biobed has also reduced the risk of 404 point source surface water pollution by removing reliance upon a manually operated isolation value

405 to prevent contaminated washings discharging directly into a farm pond. No evidence of seasonality 406 in the efficiency of pesticide removal was detected, nor was there any evidence of a decline in 407 biobed performance over the two-year monitoring period. However, elevated pesticide 408 concentrations at 90 cm depth within the drainage field potentially indicate an accumulation of 409 pesticide residues deeper within the soil profile which could pose a risk to groundwater quality. 410 Nevertheless, the results presented here clearly demonstrate the effectiveness of a three-stage onfarm biobed at reducing pesticide residues in substantial volumes of contaminated water generated 411 412 from machinery washing on a large, commercial arable farm.

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424 **References**

- Arias-Estévez, M., López-Periago, E., Martínez-Carballo, E., Simal-Gándara, J., Mejuto, J.C., GarcíaRío, L., 2008. The mobility and degradation of pesticides in soils and the pollution of
 groundwater resources. Agriculture, Ecosystem and Environment 123, 247–260. DOI:
 10.1016/j.agee.2007.07.011.
- Arnot, J.A., Gobas, F.A.P.C., 2006. A review of bioconcentration factor (BCF) and bioaccumulation
 factor (BAF) assessments for organic chemicals in aquatic organisms. Environmental Reviews 14,
 257-297. DOI: 10.1139/a06-005.
- Bending, G.D., Friloux, M., Walker, A., 2002. Degredation of contrasting pesticides by white rot fungi
 and its relationship with ligninolytic potential. FEMS Microbiology Letters 212, 59-63. DOI:
 10.1111/j.1574-6968.2002.tb11245.x.

Blacquiere, T., Smagghe, G., van Gestel, C.A., Mommaerts, V., 2012. Neonicotinoids in bees: a review
on concentrations, side-effects and risk assessment. Ecotoxicology 21, 973-992. DOI:
10.1007/s10646-012-0863-x.

- 438 Carter, A.D., 2000. How pesticides get into water and proposed reduction measures. Pesticide
 439 Outlook 11, 149-157.
- Castillo, M.P., Torstensson, L., 2007. Effect of biobed composition, moisture, and temperature on the
 degredation of pesticides. Journal of Agricultural and Food Chemistry 55, 5725-5733. DOI:
 10.1021/jf0707637.
- Castillo, M.P., Torstensson, L., Stenström, J., 2008. Biobeds for environmental protection from
 pesticide use a review. Journal of Agricultural and Food Chemistry 56, 6206-6219. DOI:
 10.1021/jf800844x.
- Clarke, J.H., Wynn, S.C., Twining, S.E., 2011. Impact of changing pesticide availability. Aspects of
 Applied Biology 106, 263-267. DOI:
- 448 Connell, D.W., 1988. Bioaccumulation behaviour of persistent organic chemicals with aquatic
 449 organisms. Reviews of Environmental Contamination and Toxicology 102, 117-154. DOI:
 450 10.1007/978-1-4612-3810-2_3.
- 451 DeLorenzo, M.E., Scott, G.I., Ross, P.E., 2001. Toxicity of pesticides to aquatic microorganisms: a
 452 review. Environmental Toxicology and Chemistry 20, 84-98. DOI: 10.1002/etc.5620200108.
- De Wilde, T., Spanoghe, P., Debaer, C., Ryckeboer, J., Springael, D., Jaeken, P., 2007. Overview of onfarm bioremediation systems to reduce the occurrence of point source contamination. Pest
 Management Science 63, 111-128. DOI: 10.1002/ps.1323.
- Environment Agency, 2007. Guidance on using a lined biobed to dispose of agricultural waste
 consisting of non-hazardouse pesticide solutions or washings (Exemption 52). Bristol, England.
- 458 Environment Agency, 2014. Pesticide monitoring in catchment sensitive farming (CSF) river 459 catchments: 2006-2013. Bristol, England.
- Ferris, I.G., Lichtenstein, E.P., 1980. Interactions between agricultural chemicals and soil microflora
 and their effects on the degradation of [C¹⁴]-parathion in a cranberry soil. J Agric Food Chem 28,
 1011-1019.
- Fogg, P., Boxall, A., Walker, A., Jukes, A., 2003a. Pesticide degradation in a 'biobed' composting
 substrate. Pest Manag Sci 59, 527-537. DOI: 10.1002/ps.685.
- Fogg, P., Boxall, A., Walker, A., 2003b. Degradation of pesticides in biobeds: the effect of
 concentration and pesticide mixtures. J Agric Food Chem 51, 5344–5349.
- Fogg, P., Boxall, A., Walker, A., Jukes, A., 2004. Degradation and leaching potential of pesticides in
 biobed systems. Pest Manag Sci 60, 645-654. DOI: 10.1002/ps.826.
- Jess, S., Kildea, S., Moody, A., Rennick, G., Murchie, A.K., Cooke, L.R., 2014. European Union policy on
 pesticides: implications for agriculture in Ireland. Pest Manag Sci 70, 1646-1654. DOI:
 10.1002/ps.3801.
- Karanasios, E., Tsiropoulos, N.G., Karpouzas, D.G., Ehaliotis, C., 2010. Degradation and adsorption of
 pesticides in compost-based biomixtures as potential substrates for biobeds in southern
 Europe. Journal of Agricultural and Food Chemistry 58, 9147-9156. DOI: 10.1021/jf1011853.
- 475 Lewis, M.A., 2011. Borehole drilling and sampling in the Wensum Demonstration Test Catchment.
 476 British Geological Survey Commissioned Report, CR/11/162, pp. 38.
- 477 Lewis, K.A., Tzilivakis, J., Warner, D., Green, A., 2016. An interational database for pesticide risk
 478 assessments and management. Human and Ecologcial Risk Assessment: An International
 479 Journal. DOI: 10.1080/10807039.2015.1133242.
- 480 Natural England, 2014. Catchment sensitive farming: evaluation report phases 1 to 3 (2006-2014).
 481 Worcester, England. ISBN: 978-1-78367-155-7.

- 482 Oerke, E.C., Dehne, H.W., 2004. Safeguarding production—losses in major crops and the role of crop
 483 protection. Crop Protection 23, 275-285. DOI: 10.1016/j.cropro.2003.10.001.
- 484 Oerke, E.C., 2005. Crop losses to pests. J Agr Sci 144:31–43. DOI:10.1017/S0021859605005708.
- Omirou, M., Dalias, P., Costa, C., Papastefanou, C., Dados, A., Ehaliotis, C., Karpouzas, D.G., 2012.
 Exploring the potential of biobeds for the depuration of pesticide-contaminated wastewaters
 from the citrus production chain: laboratory, column and field studies. Environmental Pollution
- 488 166, 31-39. DOI: 10.1016/j.envpol.2012.03.001.
- Outram, F.N., Lloyd, C.E.M., Jonczyk, J., Benskin, C.M.H., Grant, F., Perks, M.T., Deasy, C., Burke, S.P.,
 Collins, A.L., Freer, J., Haygarth, P.M., Hiscock, K.M., Johnes, P.J., Lovett, A.L., 2014. Highfrequency monitoring of nitrogen and phosphorus response in three rural catchments to the
 end of the 2011–2012 drought in England. Hydrology and Earth System Sciences 18, 3429-3448.
 DOI: 10.5194/hess-18-3429-2014.
- 494 Pimentel, D., 2005. Environmental and economic costs of the application of pesticides primarily in
 495 the United States. Environ Dev Sus 7:229–252. DOI: 10.1007/s10668-005-7314-2.
- 496 Pinto, A.P., Rodrigues, S.C., Caldeira, A.T., Teixeira, D.M., 2016. Exploring the potential of novel 497 biomixtures and Lentinula edodes fungus for the degradation of selected pesticides. Evaluation 498 for use in biobed systems. Sci Total Environ 541, 1372-1381. DOI: 499 10.1016/j.scitotenv.2015.10.046.
- Popp, J., Pető, K., Nagy, J., 2013. Pesticide productivity and food security. A review. Agronomy for
 Sustainable Development 33, 243-255. DOI: 10.1007/s13593-012-0105-x.
- Reichenberger, S., Bach, M., Skitschak, A., Frede, H.G., 2007. Mitigation strategies to reduce
 pesticide inputs into ground- and surface water and their effectiveness: a review. Sci Total
 Environ 384, 1-35. DOI: 10.1016/j.scitotenv.2007.04.046.
- Schwarzenbach, R.P., Egli, T., Hofstetter, T.B., von Gunten, U., Wehrli, B., 2010. Global Water
 Pollution and Human Health. Annual Review of Environment and Resources 35, 109-136. DOI:
 10.1146/annurev-environ-100809-125342.
- 508 Spliid, N.H., Helweg, A., Heinrichson, K., 2006. Leaching and degredation of 21 pesticides in a full-509 scale model biobed. Chemosphere 65, 2223-2232. DOI: 10.1016/j.chemosphere.2006.05.049.
- Torstensson, L., 2000. Experiences of biobeds in practical use in Sweden. Pesticide Outlook 11, 206211. DOI: 10.1039/b008025j.
- Vischetti, C., Monaci, E., Cardinali, A., Casucci, C., Perucci, P., 2008. The effect of initial
 concentration, co-application and repeated applications on pesticide degradation in a biobed
 mixture. Chemosphere 72, 1739-1743. DOI: 10.1016/j.chemosphere.2008.04.065.
- 515 Whitehorn, P.R., O'Connor, S., Wackers, F.L., Goulson, D., 2012. Neonicotinoid pesticide reduces
 516 bumble bee colony growth and queen production. Science 336, 351-352. DOI:
 517 10.1126/science.1215025.
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Table 1: Summary of the 15 pesticides analysed in the Manor Farm biobed, Salle, which were either regularly used, had high input concentrations (>100 μ g L⁻¹) or are CSF key indicator pesticides. Typical physico-chemical characteristics derived from Lewis et al. (2016).

Pesticide	Formula	2D Structure	Туре	Primary Crop Use	Soil Sorption Coefficient (K _{oc} mL g ⁻¹)	Solubility in Water (mg L ⁻¹)	Half Life in Field DT ₅₀ (days)
Propyzamide	C ₁₂ H ₁₁ Cl ₂ NO		Grass/broadleaf herbicide	Oilseed rape/field beans	840 (Slightly mobile)	9 (Low)	56 (Moderately persistent)
Ethofumesate	C ₁₃ H ₁₈ O ₅ S		Grass/broadleaf herbicide	Sugar beet	55-500 (Moderately mobile)	50 (Moderate)	37.8 (Moderately persistent)
Bromoxynil	C ₇ H ₃ Br₂NO	Br HO→−C≡N Br	Broadleaf herbicide	Cereals	302 (Moderately mobile)	90 (Moderate)	8 (Non-persistent)
Metsulfuron- methyl	C ₁₄ H ₁₅ N ₂ O ₆ S		Grass/broadleaf herbicide	Cereals	120-320 (Moderately mobile)	2,790 (High)	13.3 (Non-persistent)
Chlorotoluron	C ₁₀ H ₁₃ CIN ₂ O	CI NH N	Grass/broadleaf herbicide	Cereals	196 (Moderately mobile)	74 (Moderate)	34 (Moderately persistent)
Chloridazon	C ₁₀ H ₈ CIN ₃ O		Broadleaf herbicide	Sugar beet	120 (Moderately mobile)	422 (Moderate)	34.7 (Moderately persistent)
Carbetamide	$C_{12}H_{16}N_2O_3$		Grass/broadleaf herbicide	Oilseed rape	89 (Moderately mobile)	3,270 (High)	8 (Non-persistent)

Fluroxypyr	$C_7H_5Cl_2FN_2O_3$		Broadleaf herbicide	Cereals	74 (Mobile)	6,500 (High)	51 (Moderately persistent)
МСРА	C₀H₀ClO₃	CI-CO-O-OH	Broadleaf herbicide	Cereals	74 (Mobile)	29,390 (High)	25 (Non-persistent)
Metazachlor	C ₁₄ H ₁₆ CIN ₃ O		Grass/broadleaf herbicide	Oilseed rape	54 (Mobile)	450 (Moderate)	6.8 (Non-persistent)
Mecoprop	$C_{10}H_{11}CIO_3$	O O O O O O O O O	Broadleaf herbicide	Cereals	47 (Mobile)	250,000 (High)	8.2 (Non-persistent)
2,4-D	C ₈ H ₆ Cl ₂ O ₃	CI O O O	Broadleaf herbicide	Cereals	39.3 (Mobile)	24,300 (High)	28.8 (Non-persistent)
Triclopyr	C ₇ H ₄ Cl ₃ NO ₃		Broadleaf herbicide	Cereals	27 (Mobile)	440 (Moderate)	30 (Moderately persistent)
Clopyralid	C ₆ H ₃ Cl ₂ NO ₂	CI N OH	Broadleaf herbicide	Cereals/oilseed rape	5 (Very mobile)	143,000 (High)	11 (Non-persistent)
Dicamba	C ₈ H ₆ Cl ₂ O ₃		Broadleaf herbicide	Cereals	2 (Very mobile)	250,000 (High)	3.9 (Non-persistent)

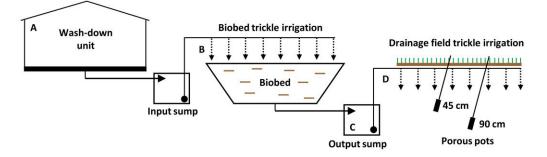
Table 2: Mean concentration data for 15 pesticides which were either regularly used, had high
 input concentrations (>100 μg L⁻¹) or are CSF key indicator pesticides. Data are for the period
 November 2013 to November 2015. The efficiency of the biobed sumps refers to the reduction
 in pesticide concentration between the input and output sumps. The efficiencies of the porous
 pots reflect the reductions in pesticide concentration between the output sump and the 45 cm
 and 90 cm porous pots. Missing values relate to non-detected pesticides.

Pesticide	Biobed Sump Mean Concentration ($\mu g L^{-1}$)			Porous Pot Mean Concentration (μg L ⁻¹)				
Pesticide	Input	Output	Efficiency	45 cm	Efficiency	90 cm	Efficiency	
			(%)		(%)		(%)	
Propyzamide	2551.3	60.0	97.6	-	-	-	-	
Chloridazon	2547.7	81.9	96.8	-	-	-	-	
Triclopyr	958.5	32.8	96.6	1.2	96.3	2.5	92.4	
Ethofumesate	26935.1	980.9	96.4	-	-	-	-	
Chlorotoluron	150.4	6.9	95.4	-	-	-	-	
Bromoxynil	167.3	11.3	93.2	1.1	90.3	1.6	85.8	
2,4-D	2944.9	213.7	92.7	2.2	99.0	6.5	97.0	
Mecoprop	803.7	112.7	86.0	3.0	97.3	6.6	94.1	
MCPA	30.4	4.8	84.2	1.1	77.1	1.6	66.7	
Fluroxypyr	1162.0	224.6	80.7	9.3	95.9	16.0	92.9	
Dicamba	223.5	43.8	80.4	9.1	79.2	13.9	68.3	
Carbetamide	15.3	3.0	80.4	-	-	-	-	
Clopyralid	1025.5	238.1	76.8	5.5	97.7	16.2	93.2	
Metsulfuron-methyl	32.9	8.1	75.4	-	-	-	-	
Metazachlor	5561.0	1754.9	68.4	-	-	-	-	

Table 3: Approximate construction costs (including labour) for the Manor Farm biobed installed in 2013.

Component	Area	Cost		
Component	(m²)	(£)	(£ m ⁻²)	
Sprayer wash-down area	270	90,454	335	
Biobed	49	4311	88	
Drainage field	200	1684	8	
Matrix replenishment after 2 years	49	378	8	
	Total cost	96,827		

13 Figures



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Figure 1: Schematic of the biobed unit installed at Manor Farm, Salle. Letters refer to the photographs in Figure 2.

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Figure 2: Images of the biobed facility installed at Manor Farm, Salle. (A) Pesticide sprayer inside the machinery wash-down unit during construction; (B) biobed operational area (7 m x 7 m) with the completed enclosed wash-down unit in the background; (C) biobed output sump and trickle irrigation system during construction; (D) drainage field trickle irrigation area, with porous pot outlets located underneath terracotta pots.

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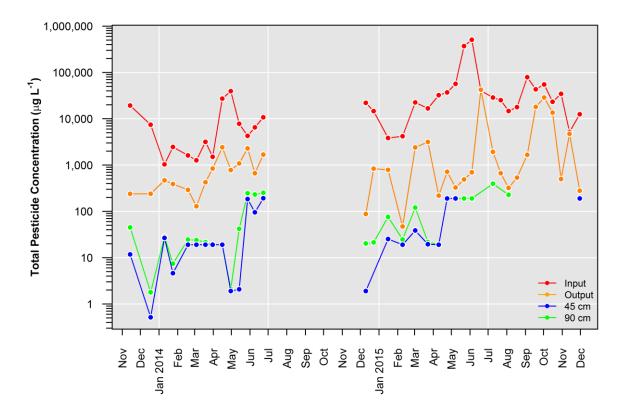




Figure 3: Total pesticide concentrations recorded in the input and output sumps and in the drainage
field porous pots (45 cm and 90 cm depth) between November 2013 and November 2015.

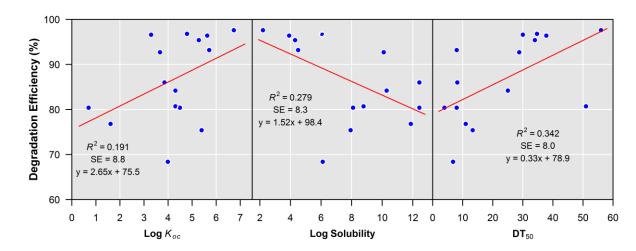


Figure 4: Linear regression relationships between biobed removal efficiency at the output sump and
the typical physico-chemical properties of the 15 key pesticides monitored. Physico-chemical
properties derived from Lewis et al. (2016).