Comparison of technical and systems-based approaches to managing pesticide contamination in surface water catchments

Martha L. Villamizar[a], Chris Stoate[b], Jeremy Biggs[c], Carol Morris[d], John Szczur[b], Colin D. Brown[a]*

[a] Department of Environment & Geography, University of York, Heslington, York, YO10 5NG, UK

[b] The Game & Wildlife Conservation Trust, Allerton Project, Loddington, Leicestershire, LE7 9XE, UK

[c] Freshwater Habitats Trust, Bury House, North Place, Oxford, OX3 9HY, UK

[d] School of Geography, University of Nottingham, Clive Grainger Building, University Park, Nottingham, NG7 2RD, UK

* Corresponding author: Department of Environment & Geography, University of York, Heslington, York, YO10 5NG, UK; colin.brown@york.ac.uk

Abstract

Diffuse pollution of surface waters by herbicides remains a problem despite 25 years of research into mitigation approaches. This study adopts the grassweed herbicide propyzamide as a focus to compare the efficacy of technical, field-scale, interventions with systems-based cropping solutions in a 900 ha headwater catchment on heavy clay soils. Catchment monitoring was combined with modelling of land management options using SWAT and semi-structured discussions with farmers. Vegetated buffers are the main mitigation in the catchment at present, and these are estimated to be halving propyzamide concentrations in the headwater stream. Increasing vegetated buffers to 20 m width around all water courses would be the most effective technical intervention. Collaboration between farmers to ensure differentiated application timings would be ineffective without precise forecasting to avoid application soon before storm events. Downstream pesticide limits could only be met by restricting the area of land treated with propyzamide, requiring a switch away from oilseed rape cultivation. This restriction was not acceptable to farmers who noted the lack of enablers for coordination between landowners and the need for pesticide targets that are specific to headwater catchments.

Keywords

Highlights

- Headwater catchments can be subject to intense pressure from single pollutants

- Existing technical, field-scale interventions halved diffuse herbicide pollution

- Systems-based solutions are most effective in reducing diffuse pollution further

- Mechanisms are required to deliver effective coordination between landowners

- Pesticide pollution targets specific to headwaters will aid negotiation with farmers

1. Introduction

Surface water contamination by pesticides following agricultural use remains a widespread and important environmental problem. Soil-applied herbicides are a particular source of contamination because they are often applied when the soil is at or close to field capacity and because they need some degree of mobility and persistence in soil to allow uptake into the roots of target weeds. Transfer of herbicides from treated land to adjacent water courses is primarily via overland flow (Burgoa and Wauchope, 1998) and subsurface drainage (Brown and van Beinum, 2009); transfer via both pathways is strongly influenced by rainfall patterns following application, soil type, agronomic practices and the degradation and sorption properties of the herbicide.

Pesticide contamination of surface waters has been recognised and legislated against for more than 25 years, and this has generated a large body of research to investigate mitigation approaches. Agronomic options such as non-inversion tillage and vegetated buffer strips are known to be effective to reduce transfer in overland flow (Reichenberger et al., 2007). In contrast, there are very limited options for reducing transfer in subsurface drains, particularly on heavy clay soils where preferential flow pathways can bypass the bulk soil and provide direct connection between the upper soil layers and the drainage system (Brown and van Beinum, 2009). Most of the research has focused on technical mitigation approaches that are applied either in-field (e.g. changes to tillage practices or use of cover crops) or at edge of field (e.g. installation of vegetated buffer strips or detention ponds). There has been comparatively little investigation of systems approaches applicable over larger areas, such as reducing the cultivation of crops associated with problematic herbicide applications. Water quality programmes applied at catchment scale have demonstrated effective reduction in pesticide contamination associated with point sources such as that associated with handling concentrated pesticide products in the farmyard (Kreuger & Nilsson, 2001). In contrast, contamination from diffuse sources has proved difficult to control with conventional agri-environment schemes (Jones et al., 2017), leaving a significant burden on the water industry to monitor and clean up water intended for drinking supplies.

Given that existing mitigation has only partially reduced concentrations of pesticides in surface waters, the aim of this research was to work alongside farmers to design and quantify the effectiveness of more ambitious mitigation and cropping systems approaches applied across a headwater catchment and then to assess the acceptability of measures. To do this we

used propyzamide as a case study compound and worked within a catchment dominated by heavy clay soils where all arable land is artificially drained. Propyzamide (3,5-dichloro-N-(1,1-dimethyl-2-propynyl)benzamide, CAS 23950-58-5) is a residual benzamide herbicide that was introduced in 1969 by Rohm & Haas Co. (now Dow AgroSciences) for the selective control of annual and broad-leaved weeds in a range of crops (Turner, 2018). Within our study catchment, propyzamide is primarily applied in autumn and winter to control blackgrass in oilseed rape (OSR) and field beans. This pattern is mirrored nationally, and use of propyzamide in the UK has increased alongside an increased cultivation of OSR with 199 tonnes of the herbicide applied to 261,000 ha of land in 2016 (Garthwaite et al., 2017). Transport of propyzamide to surface waters is exacerbated by the recommendation that application to OSR and winter field beans takes place when soil temperature falls below $10^{\circ}C$ and when there is sufficient soil moisture for plant uptake; these conditions favour persistence and mobility of herbicides in soil. Propyzamide is frequently measured at relatively high concentrations in drainflow and surface water catchments in the UK during the winter. For example, Tediosi et al. (2012) found a maximum propyzamide concentration from a field drain of 56 µg/L in a clay headwater tributary of the Upper Cherwell catchment in the UK. Propyzamide is one of seven compounds included in a pesticide contamination indicator for UK surface waters (Environment Agency, 2014) and river monitoring for six vulnerable catchments in England (2006-2012) showed 2-7% of all samples contained residues of propyzamide greater than 0.1 µg/L (Environment Agency, 2012). Although there are no known negative environmental or human health impacts of propyzamide at the concentrations found in water, the compound is relatively difficult to remove via treatment of water abstracted for drinking purposes. Thus, regular exceedance of the statutory 0.1 µg/L limit required for drinking water supply has put this herbicide at risk of withdrawal or restriction, and this is a key concern to farmers who rely on it for blackgrass control.

We applied a multi-disciplinary approach combining a programme of catchment monitoring, physical modelling of the catchment and social science methods to investigate the efficacy of approaches to catchment management ranging from technical in-field interventions to full systems-based cropping solutions. A list of potential strategies that would reduce concentrations in the headwater stream was developed with farmers and the pesticide manufacturer (Dow AgroSciences). Strategies included reducing the oilseed rape area and introducing hybrid barley as a competitive crop to limit blackgrass development, adopting riparian buffer strips, reducing tillage operations to ensure soil stability, mapping soil

compaction across fields and through the soil profile, and sharing local soil moisture data in real time to guide timing of herbicide applications and soil management. Our approach includes the use of modelling to understand the factors driving pesticide contamination of the stream and to investigate the impact of possible mitigation measures. Pesticide management options were then discussed with stakeholders to evaluate compatibility with farm business plans and to identify viable options for agricultural best management practices (BMPs).

2. Material and methods

2.1. Study area and catchment monitoring

This research is part of the Water Friendly Farming (WFF) project (Biggs et al., 2016), a Before-After-Control-Impact experiment assessing the effectiveness of mitigation measures to protect freshwater habitats and the ecosystem services they provide in agricultural landscapes, whilst maintaining profitable farming. The study area comprises the Stonton Brook headwater (catchment area 7.7 km^2) in the upper Welland catchment located in Leicestershire, UK (Fig. 1a). Water quality monitoring has been undertaken continuously at the catchment outlet since 2012. The Stonton Brook catchment is intensively tilled and drained with high connectivity to the river system. Slope is generally steep with 78% of the catchment area steeper than 4°, and altitude ranges between 216 and 123 m above sea level (Fig. 1b). Approximately 97% of the land is on heavy clays of the Hanslope association or clay loams of the Ragdale and Wickham associations, with a small area of sandy silt loams of the Wick association in the south-west (Fig. 1c). The land cover is mainly grassland (40%) and arable (52%), comprising rotations of winter cereals and OSR with some field beans. There is considerable variation in farm size and tenure arrangements, including farms that are wholly owned and farmed in-hand, rented land, and various share farming and contract farming arrangements. Most farms have agri-environment scheme agreements which include riparian buffer strips to protect water.

Stream water depth (in m) was monitored every 15 min at the catchment outlet (UK grid reference: SK748000) and then converted into stream flow (m^3/s) using a flow rating curve generated for the catchment. Hourly weather data (including rainfall, wind speed, solar radiation, relative humidity and air temperature) were recorded by a meteorological station at

Skeffington (Meteoblue, 2018) (Fig 1b, SK744027, 201 m above sea level) located at the north of the Stonton Brook catchment.

Water samples were collected at the catchment outlet every two days during autumn and winter from 2013 to 2017. Samples (300 mL) for analysis of propyzamide were extracted and concentrated using solid phase extraction. Oasis® HLB 6cc (200 mg) cartridges were conditioned with 5 mL of acetonitrile followed by 5 mL of ethyl acetate. Samples of 300 mL volume were passed through the cartridges under vacuum at a flow rate of 1 mL/min by a vacuum pump. Cartridges were then dried under vacuum for 45 minutes and eluted with 5 mL of acetonitrile followed by 5 mL of ethyl acetate and 2 mL of acetone. The organic phase was evaporated to dryness under nitrogen and redissolved in 1 mL of ethyl acetate prior to GC-MS analysis using a Clarus 680 gas chromatograph and a Clarus 600C mass spectrometer (Perkin Elmer, UK). Samples were injected splitless onto an Elite-5MS column (30 m x 0.25 m, i.d. 0.25 µm, Perkin Elmer, UK), eluted with helium carrier gas at 20 mL/min under a temperature regime ramping from 40 to 270ºC and quantified using ion 173. The limit of quantification was 0.008 µg/L.
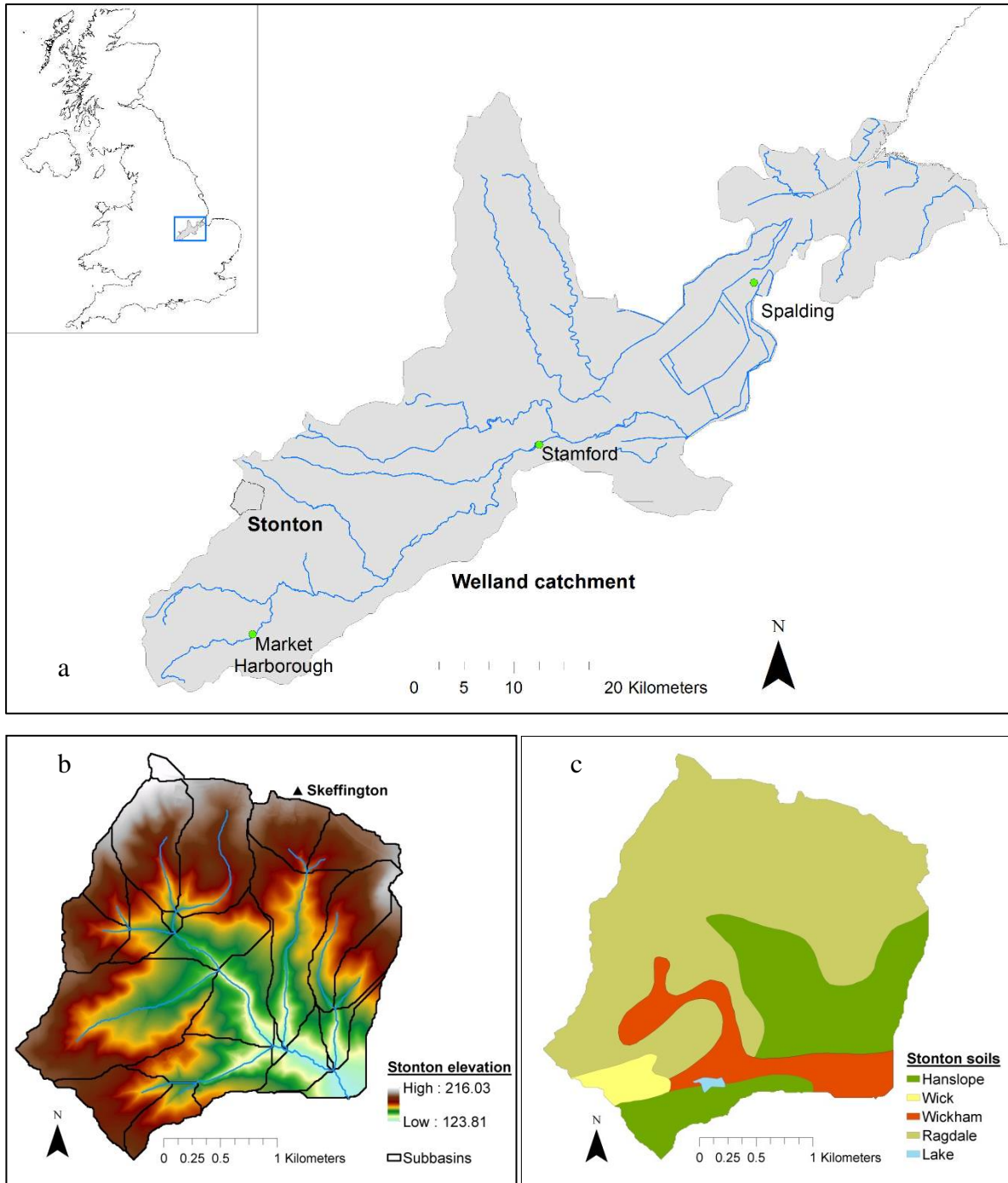
Fig. 1. a) Location of the Stonton Brook headwater catchment within the Welland river basin; b) topography (Intermap Technologies 2009), stream network, meteorological station (Skeffington) (Meteoblue, 2018), and model sub-basins; and c) map of soil associations (Cranfield University, 2014).

2.2. SWAT model

The Soil and Water Assessment Tool (SWAT; Arnold et al., 1998; version SWAT 2012 rev. 664) was used to simulate stream flow, pesticide concentration in water and mitigation

measures to study their impact in reducing diffuse pollution by propyzamide. SWAT is a physically based hydrology and water quality model, designed to estimate impacts of land management practices on water quality (including pesticides, nutrients and sediments) in complex watersheds. Full details of the model description and underpinning equations are reported in Neitsch et al. (2005). SWAT divides the catchment area into sub-catchments and each of them is further divided into hydrological response units (HRUs) which are defined as areas of land with the same soil, land use (cropping), slope and agronomic management that are assumed to behave as a homogenous unit in the model (Neitsch et al., 2005). The hydrologic routines within SWAT account for precipitation (including snow fall and melt), evaporation, infiltration, plant uptake, surface flow, lateral flow, drain flow, percolation, channel transmission losses, channel routing and shallow aquifer and deep aquifer recharge. Surface runoff is simulated on a daily time scale using the Soil Conservation Service curve number method (Mishra and Singh, 2003). Tile drainage occurs when the water table reaches above the depth at which tile drains are located (Neitsch et al., 2011).

Effects of arable cultivation can be simulated within SWAT by specifying sequences of cultivation actions at the HRU level, each with a defined mixing depth and efficiency that will redistribute any resident pesticide in the soil layer. Cultivation also acts to modify the runoff curve number, thus influencing surface runoff in response to rainfall. Vegetated filter strips are also assigned at HRU level and these act to reduce the volume of surface runoff as a function of runoff loading to the strip and saturated hydraulic conductivity; trap sediment as a function of sediment loading to the strip and runoff reduction; and trap pesticides as a function of the width of the filter strip (Neitsch et al., 2011).

Pesticide is applied at the HRU level with options for soil, foliar, and incorporated treatments. SWAT incorporates descriptions of pesticide fate processes including wash-off from treated crops, sorption to soil and sediments, degradation, leaching and lateral movement with surface runoff and lateral flow. Partition of pesticide between sorbed compound and that dissolved in soil pore water is calculated for a linear sorption coefficient. Dissolved pesticide is available for transport in surface runoff (upper 10 mm of soil only), lateral flow or vertical percolation via homogeneous mixing with the moving volume of water (Neitsch et al., 2011).

2.3. Model parameterisation

The catchment was delineated in ArcSWAT (version 2012.10_2.18 build 3552) using a NextMap Britain 5m digital elevation model (Intermap Technologies 2009) (Fig. 1b), a land use map including farm fields boundaries, and a soil map (1:250,000 scale) (Cranfield University, 2014) for the study area. The land use map was generated in ArcGIS 10.2 using the Land Cover Map 2007 (Morton et al., 2011), an aerial image of the study area, and a field cropping survey. Spatial slope data were classified into four ranges (0-4%, 4-8%, 8-12% and >12%) within the model. The catchment was finally defined by 21 sub-catchments and 218 hydrological response units.

Hourly weather data recorded at the meteorological station in Skeffington (Meteoblue, 2018) (Fig. 1b) were converted to average daily input data for the model. Soil properties were determined from the NSRI database (Cranfield University, 2014). Tile drains at a depth of 75 cm below the surface were included for all arable land located on clay soils (Ragdale, Hanslope and Wickham associations). The time to drain soils from saturation to field capacity in the model was set to 24 hours and the lag between water entering and exiting the tile drainage system was set to 10 minutes. Soil and crop management practices (e.g. tillage, pesticide and fertiliser application, crop rotation and filter strips) were defined within the model according to information on agronomic practices on the Game and Wildlife Conservation Trust farm which is adjacent to the study catchment. All arable land was set to conventional tillage within the model with inversion ploughing followed one week later by harrowing and with 95 and 20% mixing efficiency to 150 and 25 mm depth for the two operations, respectively. An aerial image of the catchment was used to define the width of edge-of-field filter strips between cropped areas and stream reaches; widths across the catchment between 2 m and 20 m.

Propyzamide is a residual herbicide for the control of a wide range of weeds in winter OSR and winter field beans. It is applied from when three crop leaves emerge and when soil temperature falls below 10°C; this is usually in November but can extend up to the end of January. Timing of propyzamide application was set to 1st November except where evidence from stream monitoring for a range of pesticides indicated otherwise; application was brought forward where propyzamide was detected earlier than the start of November, and it was delayed where other pesticides but not propyzamide were detected in storm waters generated after the start of November. We assumed that all oilseed rape and field beans were treated with propyzamide applied to the soil surface at the maximum label rate of 0.84 kg a.s./ha, except

where evidence from water monitoring data indicated that an alternative herbicide such as carbetamide had been substituted; this was the case in 2013/14 and 2014/15 where 16 and 23%, respectively, of the treated area was estimated to be treated with carbetamide instead of propyzamide. Physico-chemical parameters for propyzamide were taken from the pesticide properties database (Lewis et al., 2015), with solubility 9 mg/L, organic-carbon partition coefficient 840 mL/mg, and half-life for degradation in soil 47 days.

2.4. Modelling procedure

The SWAT calibration and uncertainty program (SWAT-CUP) (Abbaspour et al., 2007) was used for model sensitivity analysis, calibration and validation using a multiple regression system with Latin hypercube sampling and with the Nash-Sutcliffe model efficiency (NSME) as objective function. Relative sensitivities of 16 hydrology parameters that are considered to be uncertain were assessed in a preliminary step, then calibration of flow simulations was undertaken for the hydrological year (1st September to 31st August) 2012/13 (Table S1). Goodness-of-fit was evaluated using NS, the coefficient of determination (r^2) and percent bias (PBIAS) against the performance criteria proposed Moriasi et al., (2007). The best calibrated model for streamflow in 2012/13 was validated using data for 2013/14 and then applied to simulate streamflow and transport of propyzamide within the catchment from autumn 2013 to summer 2017. Pesticide parameters were not calibrated in the model; although modifying these parameters could deliver a closer model fit to the baseline simulation, the parameters are highly and non-linearly sensitive within the model so it was decided that interpretation of results would be more generally applicable by retaining measured database values. Finally, SWAT was used to assess the impact of mitigation measures targeting a reduction in diffuse pollution by pesticides. Alternatives in pesticide usage that were considered included: i) implementing riparian buffer strips of different widths across the catchment; (ii) using reduced (non-inversion) tillage on all arable fields by removing ploughing from the parameterisation and reducing runoff curve numbers by 2% as recommended for this change in tillage on soils with poor hydrological conditions (Rawls and Richardson, 1983); (iii) making split herbicide applications to avoid applying the maximum annual application limit at approximately the same time across all arable land; and iv) reducing OSR area in the catchment to reduce use of propyzamide and thus reduce pesticide concentrations in water to the drinking water limit of 0.1 µg/l.

2.5. Management options and farmer workshop

Several management practices might be adopted to reduce the movement of propyzamide from arable land to water. These were discussed informally with farmers and with a representative from Dow AgroSciences, the manufacturer of propyzamide, in the early stages of the research. They range from application of current 'best practice', as required by law for use of the product, to landscape-scale modification of the crop rotation which would require considerable collaboration or coordination between farmers in the catchment.

Unpublished research by Dow AgroSciences highlights the role of grass buffer strips for reducing movement of propyzamide to water via surface runoff, although this has limited effect where fields are drained. Their research also highlights the role of reduced soil disturbance, with direct drilling most likely to reduce concentrations of propyzamide in water running off arable land. Field drains are likely to be an important pathway for propyzamide movement to water, both adsorbed to fine sediment, and in solution, but the influence of direct drilling on transfer of pesticide in field drain water, is currently poorly understood. Buffer strips are already widely adopted within the study area, but they could be extended to greater widths to increase effectiveness. There is good potential to adopt reduced tillage within the catchment, with more limited possibilities to extend to direct drilling.

An alternative approach to applying all the propyzamide across the catchment in one narrow time window (normal practice) is to make early and late applications to different fields within the catchment, thereby reducing the amount of product present in the area at any one time. The implications of this approach for water quality were modelled. Such an approach would require considerable collaboration between, or coordination of, farmers.

Finally, diversifying the crop rotation and reducing the area of OSR would reduce the total amount of propyzamide applied in the catchment, but is another approach requiring collaboration between, or coordination of, farmers through policy intervention that allocates an OSR area quota to catchments and requires the adoption of different break crops. In this study, one farmer adopted Hyvido hybrid barley as an alternative to OSR. This could be an alternative break crop, relying on the vigorous above and below ground growth of this crop to suppress blackgrass as an alternative to the use of propyzamide in OSR.

A workshop involving two facilitators, three catchment farmers and a representative from Dow AgroSciences was held on 13 June 2017. The aim of the workshop was to enable discussion of

the various management options. This involved farmers considering the future potential of these approaches, based in some cases on their own experience of them, and in others on evidence presented at the workshop in the form of modelling results, soil moisture data and compaction maps. The full discussion was recorded and later transcribed. Qualitative, textual data from the workshop transcript were analysed through an inductive approach involving manual coding of the text and identification of commonly occurring themes as these emerged across the participants. Analysis of those parts of the text related to joint working was informed by a study of collaborative initiatives in agriculture (Morris and Jarratt 2016). Quotes from respondents have been selected to illustrate the themes and are presented anonymously to ensure participant confidentiality. It is acknowledged that these data provide only an indicative insight since they have been generated from one workshop.

3. Results

3.1. Monitoring

Table 1 provides a summary of areas of OSR cultivation, rainfall, flow, and maximum concentrations of propyzamide in the headwater stream. OSR cultivation varied between 3 and 27% of the total land surface, with the largest cultivation area in 2014/15 due to the pattern of block cropping, generally on a 4-year rotation. Annual and winter (November to January) rainfall were greatest in 2013/14 (annual rainfall was 130% of the long-term average) and this was mirrored in flow leaving the catchment outlet. Flow in the three months following normal application timing for propyzamide ranged between 112 and 222 mm for the four seasons monitored.

Monitoring for propyzamide showed seasonal presence each winter at the Stonton Brook outlet, with concentrations typically <0.4 μg/L, but at maximum 1.08 μg/L in autumn 2014 (Table 1). Area cultivated with OSR was used as a surrogate for total mass of propyzamide applied within the catchment; this was the dominant factor influencing the value of maximum pesticide concentrations in the catchment, and area of OSR had a much greater influence than rainfall or flow volumes (Table 1).

Table 1. Area of oilseed rape, annual and winter rainfall and streamflow, and maximum measured concentration of propyzamide in Stonton Brook for each crop year from 2013/14 to 2016/17. Area in % is calculated as percentage of the catchment area.

Parameter	2013/14	2014/15	2015/16	2016/17
Area of OSR (ha)	33	209	26	57
Area of OSR (%)	4.3	27.2	3.4	7.5
Rainfall (Sep-Aug; mm)	806	512	697	615
Rainfall (Nov-Jan; mm)	256	175	192	166
Flow (Sep-Aug; mm)	471	364	201	299
Flow (Nov-Jan; mm)	222	187	112	133
Maximum propyzamide concentration (µg/L)	0.27	1.08	n/a	0.41

OSR: oilseed rape; n/a: data not available

3.2. Model calibration and validation

A sensitivity analysis for the simulation of the stream flow was carried out as the initial step in setting up the catchment model in SWAT; parameter settings and best-fit values are provided in Table S1. The most sensitive model parameters were those controlling baseflow (including the threshold depth of water in the shallow aquifer for return flow, *GWQMN*; deep aquifer percolation fraction, *RCHRG_DP*; the time lag between the water exiting the soil profile and entering the shallow aquifer, *GW_DELAY*; and the threshold depth of water in the shallow aquifer and groundwater coefficient for the movement of water from the shallow aquifer to the unsaturated zone, *REVAPMN* and *GW_REVAP* respectively), travel times for lateral flow within the catchment (*LAT_TIME*), and the generation of surface runoff (runoff curve numbers, CN2, particularly those for bare soil, pasture, forest and urban areas) (Table S1). The simulated hydrograph generated on the basis of calibrated parameter values is shown in Fig. 2. Model calibration results for hydrology in the Stonton Brook catchment (2012/13) generally showed a good agreement in the magnitude and timing of peaks in the hydrograph, with values of NSME, r^2 and PBIAS values of 0.73, 0.73 and 4.4, respectively (Fig. S1 and Table S2). Results for the validation period (2013/14) also indicated a good performance for the prediction of stream flow with NSE, r^2 and PBIAS values of 0.73, 0.73 and -6.6, respectively. NSME values for flow simulations during the subsequent three seasons (2014-2017) ranged between 0.60 and

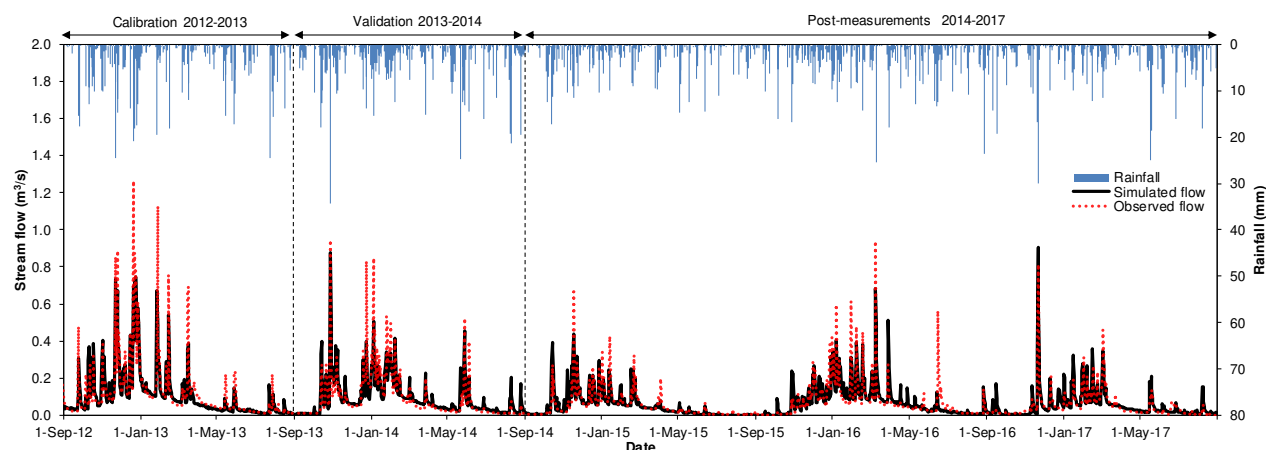0.74, indicating an acceptable flow simulation on which to base the simulation of pesticide transport.

Fig. 2. Comparison of the simulated and observed hydrograph for the calibration, validation and post-measurement periods along with the measured rainfall in Stonton Brook catchment.

Propyzamide concentrations simulated using SWAT are compared with the measured data in Fig. 3 and Table 2, whilst Table S3 gives a mass balance for pesticide export to the stream. The model was able to simulate pesticide transfer to the stream and maximum annual concentrations were generally predicted to within a factor of three. A particularly close match between model output and observed behaviour was obtained for winter 2014/15, whereas the model underestimated the maximum concentration by a factor of three for winter 2013/14 and overestimated by a factor of three for winter 2016/17. Maximum simulated concentrations were similar for 2014/15 and 2016/17 even though the OSR area in 2014/15 was almost four times larger than that in 2016/17. Around 23% of the OSR was treated with carbetamide rather than propyzamide in 2014/15. In addition, the peak concentration simulated by the model in 2016/17 was influenced by two days with heavy rainfall (17 and 33 mm) that occurred 3 weeks after application.

There were no monitoring data for the main period with expected transfers to water in autumn 2015, and no measurements were available to corroborate the small peaks predicted between February and December 2015. Deviations from observed behaviour in terms of timing of peak concentrations by a few days may be attributable to uncertainty in pesticide application dates used as input to the model. Overall, patterns and timing of propyzamide detections in the stream

were well matched and provided a good basis for investigating the effectiveness of different management strategies.
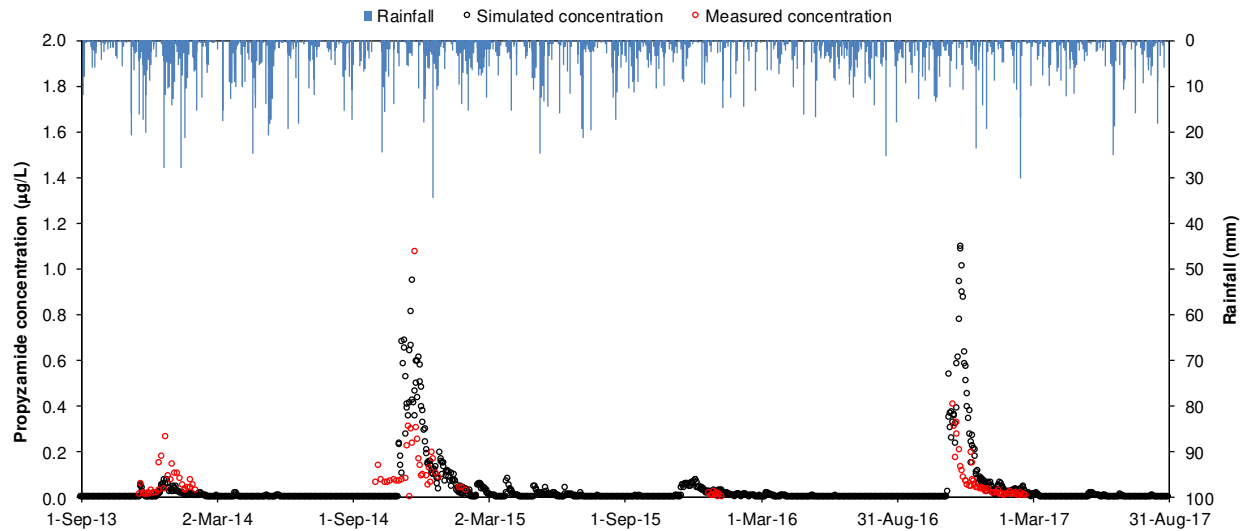

Fig. 3. Measured and simulated concentrations of propyzamide along with the daily rainfall in Stonton Brook catchment.

3.3. Effectiveness of different management options

Riparian vegetated buffer strips and modified tillage practices can be implemented by farmers to reduce transfer of pesticide and other agri-pollutants to water. The Stonton Brook headwater catchment already has a significant amount of riparian buffer and these are included within the baseline catchment simulation (Table 2). Simulations with consistent buffers across the whole catchment suggest that reducing all buffers to the statutory minimum of 2 m would lead to a 50-150% increase in maximum concentrations of propyzamide in the stream depending on season. Increasing all buffers to 20 m would deliver a reduction in concentrations, and the model indicates that this could be a 25-70% reduction compared to the current situation (Table 2). Switching all OSR fields from conventional tillage to reduced tillage had a small (5-16%) impact in reducing maximum concentrations in the stream; whilst reduced tillage would increase infiltration of rainfall into the soil profile leading to less surface runoff, water would be diverted into subsurface drains, so the net impact on pesticide transport to the stream was predicted to be relatively small.

Table 2. Measured and simulated maximum concentrations of propyzamide in Stonton Brook for four agricultural seasons. Simulated results are shown for current catchment conditions and for uniform assumptions of different widths of riparian vegetated buffer or uptake of reduced tillage.

	Maximum propyzamide concentration (μg/L)			
	2013/14	2014/15	2015/16	2016/17
Measured	0.27	1.08	n/a	0.41
Simulated (current conditions)	0.08	0.95	0.08	1.10
Simulated effect of riparian vegetated buffers:				
All set to 2 m	0.19	1.86	0.20	1.59
All set to 10 m	0.10	1.01	0.11	0.80
All set to 20 m	0.05	0.49	0.06	0.33
Simulated effect of tillage:				
Reduced tillage on all treated fields	0.07	0.88	0.07	1.04

The model was used to investigate the effect of different patterns of propyzamide application on concentrations in the stream (Fig. 4). There were no consistent differences in maximum concentrations in the stream for the four seasons simulated when propyzamide was applied on either 15th October, 1st November, or 15th November. Delaying application until December yielded smaller concentrations for 2014/15 and 2016/17, and application on 1st December was the optimal date across the four seasons. Relatively large differences in concentrations following applications on different dates (Fig. 4) were driven by subsequent rainfall patterns; however, events causing maximum concentrations were often 10-20 days after application and thus could not be anticipated by a farmer trying to determine the optimal time of application. December 2016 was particularly dry (27 mm rainfall in total), so the two December application dates for 2016/17 resulted in much smaller concentrations than applications in October or November. Splitting applications so that 50% of fields were treated on either 15th October or 1st November and the remaining 50% was treated six weeks later resulted in simulated maxima that were intermediate between best and worst for all fields treated on a single date. The split application ensures that the total mass of propyzamide in soils across the catchment would be smaller at the time of any individual event; however, it also increases the likelihood that one of the applications would be made shortly before a rainfall event that generates surface runoff and/or drainflow.
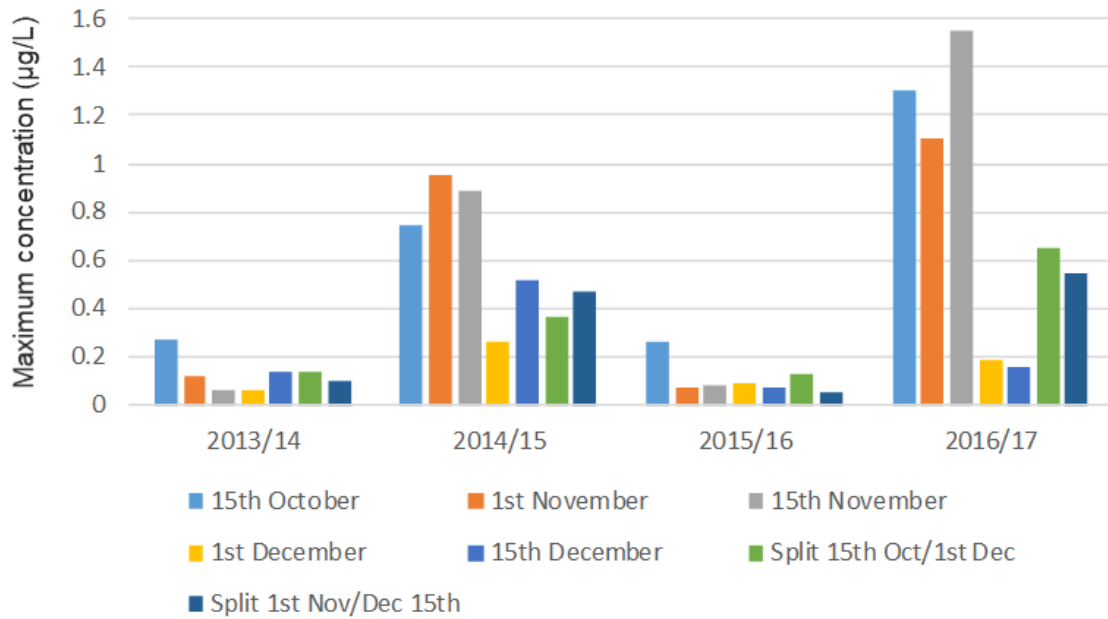
Fig. 4. Effect of application timing on maximum concentration of propyzamide simulated at the catchment outlet for four seasons. Scenarios are all fields treated at full dose at dates between 15th October and 15th December, or split treatments with 50% of fields treated on either 15th October of 1st November and the remaining 50% treated six weeks later.

Measured and simulated propyzamide concentrations were used to estimate the maximum area of OSR that could be grown in each year to deliver a maximum pesticide concentration of 0.1 µg/L in the stream at any point during the season. Results showed that with current application practice, the area of OSR would need to be reduced to ca. 2-3% of total land area to meet this target on concentrations in the stream (Table 3). Pesticide residues in water may be diluted for points further downstream if the proportion of land treated with propyzamide is smaller within the broader catchment, or if the lower catchment is less vulnerable for pesticide transfer to water. Proportionately larger areas of OSR could be grown and treated with propyzamide if this dilution effect was certain, because concentrations in the headwater could be allowed to exceed 0.1 µg/L. For example, a fivefold dilution effect might allow propyzamide-treated OSR on 10-15% of the headwater catchment. In some catchments, a small proportion of land may be particularly vulnerable to pesticide losses to water and could be targeted for any pesticide usage restrictions. This approach was found not to be applicable here because all arable fields were heavy clays with subsurface drains and with some vulnerability to surface runoff; there is a very close connectivity to surface water for all arable land via either the natural stream network or artificial ditches.

Table 3. Actual area of OSR grown plus calculations of crop area that would ensure concentrations of propyzamide in the stream did not exceed 0.1 µg/L in Stonton Brook. Calculations are made using either monitoring data or model simulations.

	2013/14	2014/15	2015/16	2016/17
Area of OSR (ha)	33	209	26	57
Area of OSR (%)	4.3	27.2	3.4	7.5
Area of OSR to deliver 0.1 µg/L using measured data	12.2	19.4	n/a	13.9
% OSR to deliver 0.1 µg/L using measured data	1.6	2.5	n/a	1.8
Area of OSR to deliver 0.1 µg/L using simulated data	43.5	22.0	33.4	5.2
% OSR to deliver 0.1 µg/L using simulated data	5.7	2.9	4.4	0.7

3.4. Farmer workshop

Farmers recognised that rainfall could vary across the catchment but thought soil moisture data could be a useful means to guide pesticide application timing if they were sufficiently local. However, data showing when the field drains were running were not thought to be useful as it was too late to make decisions about propyzamide application once drains were flowing. Farmers thought that soil compaction maps might be helpful to determine where and when deep cultivation of soil would be necessary; there was concern about the cost of obtaining the data, although Farmer B already uses a penetrometer to 30 cm before any sub-soiling or other cultivation. Buffer strips were regarded as being standard practice. "I don't think anybody would have any problems with adopting a six-metre buffer strip against any water course. People have got used to having these buffer strips now" (Farmer B).

The consensus amongst the farmers was that splitting applications across two application windows would not be viable. The long gap required between the two application windows would mean that at least one of the applications would be applied at sub-optimal conditions for maximum efficacy. Farmer A, as a contractor, needed to manage the use of his spraying equipment efficiently and feared that "the machine is going to be working elsewhere at the wrong time". Undesirable medium-term rotation effects could also be triggered, with this less efficient regime leading to "blackgrass pressure and more use of pesticides the following year"

(Farmer C). Farmer C stated that OSR is the second most profitable crop on the farm and that there is no incentive to produce grass as an alternative with low herbicide use. It would be unlikely that farmers would volunteer to not grow OSR or replace it with grass without significant financial recompense.

Farmer A's two-year wheat/OSR rotation had been starting to deliver reduced OSR yields and he had decided to introduce Hyvido hybrid barley into the rotation. This allowed earlier establishment of a following OSR crop and he had seen improved efficacy of propyzamide. He additionally used a reduced cultivation method with a customised drill to minimise the disturbance to the soil. He was startled by the beneficial effect that the hybrid barley had had on supressing blackgrass remarking that "it's staggering and I still (can't) quite pinpoint why it seems to do what it does"; hybrid barley "does not get rid of blackgrass … but it massively reduces the seed return and by massively reducing the seed return, and then hitting it with propyzamide, far more effectively (…) we're hoping when we get round to year three we're going to see a dramatically reduced level of blackgrass germinating in a crop of wheat than we would have done beforehand". Farmer C commented that this approach was good for long term sustainability because it both improved OSR yields and controlled blackgrass, which improved the whole farming system. Although Farmer A was enthusiastic about his three-year rotation with hybrid barley, this was not regarded as an option by Farmer B who uses a four-year rotation that includes spring oats and beans but not barley because of storage constraints. However, it is worth noting that the purpose of the lengthened rotations for both farmers was not primarily to do with concerns about propyzamide but rather the control of blackgrass.

The propyzamide limit required by the water company in water courses at the point of abstraction for drinking water is 0.1 µg/L and this would restrict OSR cultivation to 2-3% of the catchment area if the limit were directly transposed to the headwater catchment. Farmers were also asked to comment on whether a restriction of OSR to 8-10% of the land would be possible; this area restriction was derived by assuming that a five times larger limit of 0.5 µg/L could be applied to propyzamide concentrations in the headwater stream because this was not the point in the catchment at which water was extracted for drinking purposes. The consensus amongst the farmers was that this approach would not be viable; although the area of OSR within the catchment would be well below 10% in most years, at some point their rotations will 'clash' leading to an area of OSR in the catchment that significantly exceeds 10%. Rotations cannot be modified to meet the catchment limit without compromising profitability. Also, the

price of OSR will influence the area of it that farmers grow. So, although two of the farmers realised that next year their rotations would not clash, and one jokingly gave the other permission to "go ahead with your eighty hectares [laughter]", there was no support for possible co-ordination or collaboration to achieve a catchment limit on the area of OSR. Rather they thought that if the total area of OSR in the catchment were to be restricted, then those farmers who were disadvantaged by the limit in any year would need to be compensated financially by the water company for either not growing OSR, or for not using propyzamide on it. Farmer C thought that year-on-year variation in the area of OSR grown within the catchment would be likely to increase further in future because of the trend towards fewer, bigger farms which tend to block crop, reducing crop diversity. This could lead to the catchment area limit for OSR being exceeded for several years in succession. As a contractor, Farmer A saw that this approach would expose him to getting involved in coordinating his clients to meet the catchment OSR limits and declared firmly that "that doesn't interest me in any way, shape or form". So, there is an absence of enablers for collaboration and a major constraint is that this approach is perceived as likely to be detrimental to the farm business.

As described above, Farmer A was employing a reduced cultivation technique to establish his OSR. He has not abandoned deep cultivation, but he is not doing it every year. Strip tillage seems to result in less germination of blackgrass than disturbing all the soil and Farmer B thinks that "probably the more stable soil is holding the propyzamide better than churned up soil". He is also seeing less runoff than with non-inversion shallow tillage.

The main barrier to a full no-till system is the lengthy transition period where there is a significant drop in yield and "a serious impact on your bottom line" (Farmer A). Farmer B, who is in a transition period of strip tillage has seen a marked improvement in soil condition in the top 15 cm of soil over the past two or three years. However, he warned that it would be too "drastic" to go straight from this into no-till, but through managing the soil and improving it no-till could be achievable after "5/6/7 years of judicious soil management". Farmer C agreed that a mixture of no-till and min-till is a viable approach to improve the soil, but was concerned that there is no considered government advice about how to convert. As Farmer B pointed out, the financial risk of conversion is such that "you can't afford to experiment with (it) and get it wrong". Farmer C noted that if there really are only 100 harvests left in the soil, then this would be an incentive for farmers to "make the transition to doing something different". This recognises the long-term responsibility of farmers to manage and improve soils but also

highlights the long-term commitment required for transition to a no-till system. From a contractor's point of view, Farmer A explained that soil management depends on what the owner wants to achieve. The contractor has no opportunity to move to/invest in no-till if the landowner wants maximum yield and will get in another contractor to protect their short-term returns. However, where a farm is in hand, the owner can take a longer-term view. Farmer B drew the contrast between good husbandry of soils, "which evolves over a long, long time" and the life of a government, which is similar to the length of a normal rotation, and regretted that this prevents governments from implementing a long-term view for agriculture. Farmer B was particularly concerned about what he perceived to be a lack of research into soil management and thought that there needed to be long term trials rather than the current trend for 3 year trials.

4. Discussion

This research was framed within the continuing problems associated with pesticide contamination of surface water systems that persist despite 25 years of research into management solutions. Autumn-applied herbicides are a particular problem in the UK and the research considered propyzamide application to a vulnerable catchment with heavy clay soils to investigate the efficacy and acceptability to farmers of approaches to catchment management ranging from technical in-field interventions to systems-based cropping solutions. Results demonstrate that there is already significant management of hydrological pathways to reduce transfer of pesticides and other pollutants to water; this is evidenced, for example, in existing riparian buffer strips that intercept runoff and are predicted to roughly halve concentrations in stream water compared to the adoption of only mandatory (2-m wide) buffer strips. Technical solutions including increasing the width of buffer strips, transferring all land into non-inversion tillage, or modifying the timing of propyzamide application, all showed potential to reduce concentrations of the herbicide in the stream. However, the associated reductions were relatively small (with a maximum 25-70% reduction for 20-m buffers; Table 2) and efficacy varied year-on-year dependent both on the mitigation approach and weather conditions around time of application.

Two systems solutions were investigated with both involving coordination and/or collaboration between farmers. Splitting applications of propyzamide within the catchment so that fields were treated at distinctly different times was only partially effective because reduced overall

presence of the herbicide at any one time was offset by an increased risk of some of the applications being made soon before storm events that determine extent of transfer to water. In contrast, a strategy of modifying cropping choices to restrict the area treated with propyzamide could be highly effective. Although the farmers indicated that they would consider a collaborative approach, each of these proposed solutions suffered from at least one overwhelming constraint to collaboration. Splitting the application of propyzamide in time could lead to reduced efficacy of the product and hence to a perverse result of worse blackgrass the following year that would require increased application of propyzamide. Limiting the area of OSR within the catchment would compromise each farmer's core business and would necessitate a move away from the practice of block cropping that has become the industry norm over the last two decades. In addition, farmers could not identify any compelling enablers for either of these solutions. Nevertheless, coordination can be realised if an external facilitator is employed and gains the trust of the farmers who are being coordinated and this may go part of the way to addressing these concerns (Morris and Jarratt, 2016). The farmers' perspective of short-termism in government policy relative to agricultural investment timescales is beginning to be challenged by the development of a 25-year plan to improve the UK environment (HM Government, 2018); this targets a long-term environmental land management system based on the natural capital approach. That timescale is sufficient to mean that impacts of climate change might become relevant in determining agri-environmental policy. The UK climate projections show that climate change is expected to bring warmer and wetter winters, with fewer but more intense rain days, and hotter, drier summers (Murphy et al., 2009); it can be anticipated that these winter conditions will exacerbate the potential for transfer of pesticide to surface waters by increasing the frequency and magnitude of winter runoff and drainflow.

One of the most important findings to come out of the research is the need for achievable and evidenced targets for pesticide concentrations in headwater catchments. The farmers expressed forcefully during the workshop that they felt they were being asked to work to a demanding limit without evidence that this was necessary, contested the imposed concentration limit of 0.1 µg/L, and were of the opinion that the limit has been set at that level because it is the smallest detectable amount rather than because it has been established by research as a safe limit for human health or for the environment. Indeed, the 0.1 µg/L limit applies to individual pesticides in water supplied to the tap (European Council, 1998). It is difficult to transfer this limit to upper headwater catchments of the type considered here because pesticides in water will be subject to a range of processes (adsorption, biodegradation, dilution etc.) during transfer

downstream that will vary from catchment to catchment (Holmes et al., 2018). All surface water abstracted for drinking purposes in the UK will undergo treatment prior to supply, generally including either ozonation or passage through granular activated carbon (Evans et al., 2003) that will reduce concentrations of propyzamide further. Work to define an operational limit on raw streamwater in headwaters could help in effective discussion of the problem with landowners. Here, the reduction in OSR cultivation (to 2-3% of total land area; Table 3) that would be needed to ensure no contamination of the stream above 0.1 µg/L was completely implausible to the farmers; defining a higher limit value that accounted for downstream dilution and drinking water treatment practices could have advanced the discussion and identified a compromise consistent with both water protection and farm business plans.

5. Conclusions

This research demonstrates the value of existing technical, field-scale mitigation of surface water pollution from farming as well as the benefits of extending the approach. A broader step-change in water protection will require systems-based solutions such as changes to cropping rotations. Although we have focused on a single herbicide, our findings have considerably wider implications for multiple catchment management objectives because propyzamide shares pathways to water with other diffuse pollutants such as sediment and phosphorus which have impacts on stream ecology, sedimentation of drainage channels, and eutrophication. Our work highlights the need for pollution targets that can be applied to specific locations such as headwater catchments, but significant obstacles remain that inhibit joint working between farmers to meet environmental objectives. These obstacles can be eroded by development of a shared interest and trust between participants, availability of financial or economic incentives to stimulate joint working, and provision of resources to support facilitation and arbitration (Morris & Jarratt, 2016).

for gathering soil compaction data. We also acknowledge the contributions of Isabel Grijalvo Diego who undertook propyzamide analyses, Susanne Jarratt who helped to coordinate the farmer workshop and took the lead in analysing the qualitative data arising from the discussion, and Felicity Crotty who collected data on soil moisture content and soil compaction.

Competing interests

The authors confirm that they have no competing interests.

References

Abbaspour, K.C., Vejdani, M., Haghighat, S., 2007. SWAT-CUP Calibration and Uncertainty Programs for SWAT. Modsim 2007: International Congress on Modelling and Simulation 1603-1609.

Arnold, J.G., Srinivasan, R., Muttiah, R.S., Williams, J.R., 1998. Large area hydrologic modeling and assessment - Part 1: Model development. J. Am. Water Resour. As. 34, 73-89. https://doi.org/10.1111/j.1752-1688.1998.tb05961.x.

Biggs, J., Stoate, C., Williams, P., Brown, C., Casey, A., Davies, S., Grijalvo Diego, I., Hawczak, A., Kizuka, T., McGoff, E., Szczur, J., Villamizar Velez, M., 2016. Water Friendly Farming, Autumn 2016 Update. Freshwater Habitats Trust & Game & Wildlife Conservation Trust. 25pp. https://freshwaterhabitats.org.uk/wp-content/uploads/2016/11/Water-Friendly-Farming-update-2016.pdf Accessed 8th April 2019.

Brown, C.D., van Beinum, W., 2009. Pesticide transport via sub-surface drains in Europe. Environ. Pollut. 157, 3314-3324. https://doi.org/10.1016/j.envpol.2009.06.029.

Burgoa and Wauchope, 1995. Pesticides in surface run-off and surface waters. T.R. Roberts, P.C. Kearney (Eds.), Environmental Behaviour of Agrochemicals, 9, John Whiley and Sons, Ltd, Chichester, England, pp. 221-255.

Cranfield University, 2014. The Soils Guide, Cranfield University: Available: www.landis.org.uk.

Environment Agency, 2012. Pesticides in Catchment Sensitive Farming catchments 2006-2012. Catchment Sensitive Farming. Evidence Directorate. Environment Agency, UK.

Environment Agency, 2014. Catchment Sensitive Farming. Evaluation report: Phases 1 to 3 (2006-2014). CSF Evidence Team. Environment Agency, UK.

European Council, 1998. Council Directive 98/83/EC of 3 November 1998 on the quality of water intended for human consumption. Official Journal of the European Communities L 330 32-54.

Evans, H., Bauer, M., Goodman, N., Hague, J., Ta, T., 2003. The role of ozone in improving drinking water quality in London and Oxford. Ozone-Sci. Eng. 25, 409-416. https://doi.org/10.1080/01919510390481739.

Garthwaite, D.G., Barker, I., Ridley, A., Mace, A., Parrish, G., MacArthur, Y., Lu, Y., 2017. Pesticide usage survey report 271: Arable crops in the United Kingdom 2016. National statistics. Fera: York.

Holmes, C., Brown, C. D., Hamer, M., Jones, R., Maltby, L., Silberhorn, E., Teeter, J. S., Warne, M. & Weltje, L., 2018. Risk assessment of chemical mixtures in agricultural landscapes. Environ. Toxicol. Chem. 37, 674-689. https://doi.org/10.1002/etc.4049.

HM Government, 2018. A green future: our 25 year plan to improve the environment. Defra, London, UK, pp.151.

Intermap Technologies, 2009. NEXTMap British Digital Terrain (DTM) Model Data by Intermap. NERC Earth Observation Data Centre.

Jones, J.I., Murphy, J.F., Anthony, S.G., Arnold, A., Blackburn, J.H., Duerdoth, C.P., Hawczak, A., Hughes, G.O., Pretty, J.L., Scarlett, P.M., Gooday, R.D., Zhang, Y.S.S., Fawcett, L.E., Simpson, D., Turner, A.W.B., Naden, P.S., Skates, J., 2017. Do agri-environment schemes result in improved water quality? J. Appl. Ecol. 54, 537-546. https://doi.org/10.1111/1365-2664.12780.

Kreuger, J., Nilsson, E., 2001. Catchment scale risk mitigation experiences - key issues for reducing pesticide transport to surface waters. A. Walker (Ed.), Pesticide Behaviour in Soils and Water. British Crop Protection Council Symposium Proceedings 78, pp. 319-324.

Lewis, K.A., Green, A., Tzilivakis, J., Warner, D., 2015. The Pesticide Properties DataBase (PPDB) developed by the Agriculture & Environment Research Unit (AERU), University of Hertfordshire, 2006-2015.

Meteoblue, 2018. Skeffington weather station historic+ data. Meteoblue. https://www.meteoblue.com/en/weather/archive/export/skeffington_united-kingdom_2637767.

Mishra, S.K., Singh, V.P., 2003. Soil conservation service curve number (SCS-CN) methodology. Kluwer Academic, Dordrecht ; London.

Moriasi, D.N., Arnold, J.G., Van Liew, M.W., Bingner, R.L., Harmel, R.D., Veith, T.L., 2007. Model evaluation guidelines for systematic quantification of accuracy in watershed simulations. T. Asabe 50, 885-900.

Morris, C., Jarratt, S., 2016. SIP - Sustainable Intensification Research Platform: Case Studies of Collaborative Initiatives. University of Nottingham.

Morton, D., Rowland, C., Wood, C., Meek, L., Marston, C., Smith, G., Wadsworth, R., Simpson, I.C., 2011. Final Report for LCM2007 - the new UK Land Cover Map., Contryside Survey Technical Report No. 11/07 NERC/Centre for Ecology & Hydrology 112pp. (CEH Project Number: C03259).

Neitsch, S., Arnold, J., Kiniry, J., Williams, J., 2011. Soil and water assessment tool: Theorical documentation version 2009. Texas Water Resources Institute, Collage Station, TWRI Report No. 406. Texas, USA.

Neitsch, S., Arnold, J., Kiniry, J., Williams, J., King, K., 2005. Soil and water assessment tool theoretical documentation version 2005 Texas, USA.

Rawls, W.J., Richardson, H.H., 1983. Runoff curve numbers for conservation tillage. J. Soil Water Conserv. 38, 494-496.

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. https://doi.org/10.1016/j.scitotenv.2007.04.046.

Tediosi, A., Whelan, M.J., Rushton, K.R., Thompson, T.R.E., Gandolfi, C., Pullan, S.P., 2012. Measurement and conceptual modelling of herbicide transport to field drains in a heavy clay soil with implications for catchment-scale water quality management. Sci. Total Environ. 438 103-112. https://doi.org/10.1016/j.scitotenv.2012.08.042.

Turner, A.J., 2018. The pesticide manual. 18th edition. British Crop Protection Council, Alton, Hampshire, UK.