
Published paper
Deasy, C., Heathwaite, A.L. and Brazier, R.E. (2008) *A field methodology for quantifying phosphorus transfer and delivery to streams in first order agricultural catchments,* Journal of Hydrology, Volume 350 (3-4), 329 - 338.

A field methodology for quantifying phosphorus transfer and delivery to streams in first order agricultural catchments

C. Deasy[ab*], A.L. Heathwaite[b] and R.E. Brazier[c]

[a]*Department of Geography, University of Sheffield, Winter Street, Sheffield, S10 2TN*
[b]*Lancaster Environment Centre, Lancaster University, Lancaster, LA1 4YQ*
[c]*Department of Geography, University of Exeter, Amory Building, Rennes Drive, Exeter, Devon, EX4 4RJ*
*Corresponding author. Email address: c.deasy@lancaster.ac.uk

Abstract

An understanding of the relative importance of different hydrological pathways in phosphorus delivery from land to water is currently constrained by a lack of appropriate methods available to quantify the delivery process. New monitoring tools are needed which will provide a framework for understanding phosphorus (P) transfer and delivery at a range of scales in agricultural catchments. A field methodology incorporating the techniques of event-based, on-site observation and sampling within a flexible, non-plot based structure is described and applied to a first order stream catchment in Southern England, UK. The results show that P transfers to the stream reach monitored were dominated by inputs from one field drain, and that overland flow inputs, despite being directly connected to the stream and containing higher P concentrations (maximum 3708 $\mu g\ l^{-1}$), contributed less to the stream P flux. The processes of P transfer and delivery to the stream were complex, changing both within flow pathways and temporally over an event.

Keywords: Phosphorus; Delivery; Field Methods; Scale

Introduction

Diffuse agricultural sources are viewed as a major contributor to elevated phosphorus (P) concentrations in surface waters, particularly since control of point sources has been successfully implemented through legislation (Withers and Lord, 2002). Concerns over diffuse agricultural impacts in the UK have resulted in a considerable number of studies focussing on control of P movement from agricultural land to surface waters, particularly within the last decade (e.g. Gburek et al., 1996; Heathwaite and Dils, 2000; Kleinman et al., 2006; Kronvang et al., 2002; McDowell et al., 2001). Although there is now a wide knowledge base relating to P processes, traditionally studies have focussed on plot and catchment scale monitoring, with notable exceptions (Dils and Heathwaite, 1996; 2000; Wood *et al.*, 2005). The focus on a limited number of scales has resulted in a lack of quantitative data and process information at intermediate scales and from areas outside traditional monitoring scales. The linkages between monitoring scales, the role of connectivity in P transfer from sources to stream, and the relative importance of different hydrological pathways in P delivery are still not well-understood (Beven et al., 2005; Haygarth et al., 2005). As a consequence, the process representations and datasets on which concepts and models of P delivery are based may be inappropriate.

Although progress in model development is being made (e.g. Davison et al. this issue), development is inhibited by a lack of tools available to accurately represent and quantify P delivery across a range of scales (Heathwaite et al., 2005). Traditional monitoring research methods do not have the capacity to obtain the necessary information, and inventive monitoring strategies are needed (e.g. Harris and Heathwaite, 2005). This paper describes and demonstrates a simple monitoring methodology which can be used in small agricultural catchments to quantify P transfer and delivery and assess the relative importance of P transfer pathways and processes which are not accounted for by traditional monitoring scales.

Methodology

Field Site

The selected field site is a dairy farm in the Sem sub-catchment of the Hampshire Avon, near East Knoyle in Wiltshire (ST 880294) (Figure 1). Gently sloping hillslopes (1°) are drained by a stream channel with a catchment area of approximately 1.7 km^2. The East Knoyle stream flows into a first order tributary of the Sem, which is monitored as part of the PSYCHIC project (Jarvie *et al.*, 2005b). The soil is a clay loam (Wickham 2 soil series) developed over Kimmeridge clay. Three of the fields (fields A, B and C) are in rotation (wheat, maize, grass), while the fourth (field D) is used for permanent pasture (Figure 1). Fields A, B and C are all of medium soil fertility, with total P concentrations of 1125 mg kg^{-1} and Olsen P concentrations of 46-67 mg kg^{-1} (Withers *et al.*, 2007), while field D has an Olsen P concentration of below 20 mg l^{-1}. Each of the crop types receives P supplements in spring:

Wheat: Fertiliser 20 kg P ha^{-1}

Maize: Fertiliser 20 kg P ha^{-1}, farm yard manure 40-50 t ha^{-1} (ploughed in).

Grass: Fertiliser 20 kg P ha^{-1}, farm yard manure 25 t ha^{-1}

Permanent pasture: Farm yard manure 25 t ha^{-1}

Field C also receives dilute dirty water inputs of approximately 10000 l ha^{-1} every 2 months when soil conditions allow. Field A contained runoff plots used to monitor sediment and P transfer in hillslope flow under different cultivation practices (Withers *et al.*, 2007), but aside from an automatic raingauge, the site had no other monitoring infrastructure. East Knoyle was selected as a high risk site for P loss due to its slowly permeable clay soils, history of dairy production, poorly maintained underdrainage system, cattle poaching, proximity of hardstanding and farm buildings to the channel, and the recent introduction of maize which is highly susceptible to erosion and receives large inputs of P in manure (Environment Agency, 2002).

Approach

In order to address the gaps in P process information and data discussed above, a simple monitoring methodology was developed, which allows collection of data at scales outside the plot and catchment, some quantification of P delivery, and hence further understanding of P processes in first order agricultural catchments. The methodology is based on the integration of several approaches:

- *Event-based field observations* – the majority of P has been shown to be transferred during discrete hydrological events (Dils and Heathwaite, 2000; Jordan et al., 2005; Pionke et al., 1996). Event-based field observations are therefore an appropriate scale for targeted monitoring, and enable direct study of hydrological pathways and flow connectivity.

- *Point sampling* – in the absence of automatic samplers for streams and drains, samples need to be collected manually. Where permanent sampling structures are inappropriate, such as for monitoring overland flow down farm tracks, point sampling is the only practical option. Point sampling causes minimum disturbance to the site, it is cost-effective, and enables flexible sampling.
- *Flexible sampling structure* – the non-plot based approach prevents the problems of significant boundary effects (Wainwright et al., 2000), and allows sampling to take place where runoff actually occurs during an event.
- *High spatial and temporal resolution monitoring* – high resolution data can promote insights into spatial and temporal variability, and may provide information on catchment connectivity.
- *Consideration of point fluxes* – combination of discharge and concentration data allows quantification of P transfer and delivery, and enables comparison of the influence of different P pathways and inputs to the stream.

The methodology consists of three phases. An understanding of the nature of the site was required in order to put the event-based monitoring into context, and this was gained through the first phase, a pre-event survey, which was also used to select monitoring points and establish an in-stream baseflow level where continuous flow occurred. In the second phase, event monitoring, temporary and continuous flow pathways were selected and sampled. In the third phase, the post-event survey, residual sediment was collected and the overland flow locations monitored during the second phase were profiled.

Field Monitoring

Pre-Event Survey

A pre-event survey was carried out to identify key hydrological pathways and farm-scale connectivity routes and barriers. Mapping of the site was carried out using site observation and consideration of features such as drainflow outlets, sediment deposits and disturbance to vegetation by water, and was supported by Ordnance Survey data (http://edina.ac.uk/digimap). Monitoring points were then selected in the stream to allow event-based monitoring of differences in stream characteristics caused by stream inputs. Suitable stream monitoring locations were identified by considering the location of drain outfalls and overland flow pathways and locating monitoring points upstream and downstream of these inputs. Further monitoring points were added at appropriate intervals to increase the spatial sampling resolution to a reasonable number of sampling points. Profiles of continuous flow pathways at selected monitoring points included vertical measurements to a baseline at intervals across the channel. Water depth measurements were taken in continuous flow pathways at the locations profiled, and these measurements were later used together with the profiles to calculate an estimate of streamflow velocity and baseflow discharge.

Event monitoring

Rainfall data were collected using a Campbell ARG 100 tipping bucket raingauge to record tips of 0.2 mm depth, which were aggregated into 1 minute time series data for analysis. During an event, the location and connectivity of temporary flow pathways such as overland flow in tracks and fields and non-continuous drainflow outlets was observed. A number of water sampling locations within these pathways were selected where two pathways converged, where overland flow entered the stream, and at appropriate intervals down-track. Where the number of possible sampling locations was too large to allow monitoring of each pathway the sites were prioritised, taking into account linkage to point source areas such as hardstandings, field land use and other nutrient and sediment transfer risk features. Repeated monitoring of water depth and water sampling at the continuous-flow and temporary pathway locations selected was carried out, and depth measurements were later used with the surveyed profiles to calculate estimates of flow velocity and event discharge.

Post-Event Survey

Profiles for the temporary pathway monitoring sites selected for event monitoring were measured as for continuous flow pathways in the pre-event survey. Slope measurements of temporary pathways were taken using a clinometer, and samples of any residual sediment left in the temporary flow pathways during the event were collected.

Laboratory Analysis

Water Samples

Samples were refrigerated at 4 °C, in the polyethylene bottles used for collection, prior to analysis. Samples were analysed for Total P (TP), Total P <0.45μm ($TP_{<0.45\mu m}$) and suspended sediment (SS). For TP analysis, 12 ml aliquots of sample were digested using persulphate microwave digestion at 40 % for 45 minutes (CEM Model MDS 81D, 650 watts). Samples for $TP_{<0.45\mu m}$ were first filtered through 0.45 μm Whatman cellulose nitrate filters within 24 hours of collection. Analysis of TP concentrations was determined colorimetrically (Murphy and Riley, 1962) using flow injection analysis. For SS analysis, 250 ml samples were filtered through pre-weighed 0.45 μm Whatman nylon filters and filters were then dried at 105 °C before being re-weighed. All samples were analysed within one week of collection. The water particulate P fraction, $TP_{>0.45\mu m}$, was determined by difference ($TP_{>0.45\mu m} = TP - TP_{<0.45\mu m}$).

Soil and Sediment Samples

Soil and sediment samples of known volume were weighed, oven dried at 105 °C and then reweighed to allow calculation of bulk density and soil moisture content. Particle size distribution was determined with a laser particle size analyser (Cilas Model 940) after sieving at 600 μm, dispersion with sodium hexametadiphosphate, and organic matter removal with hydrogen peroxide. Particles larger than 600 μm were sieved and weighed manually. Samples for TP analysis were digested using the Total Kjeldahl digestion procedure. Samples were ground and sieved at 212 μm to increase the efficiency of the digestion process, and particles larger than 212 μm were discarded as P is principally associated with colloidal material. TP was then determined colorimetrically using flow injection analysis as before.

Hydraulic Analysis

Discharges for baseflow and event flow were calculated and combined with concentration data to calculate P and SS fluxes. Flow discharge was determined using pathway profile and depth sampling data to build up geometric profiles from which flow area and hydraulic radius were calculated and then applied in the following equations:

Manning equation (stream)
$$v = \frac{\left(R^{2/3}\sqrt{s}\right)}{n} \qquad (1)$$

Modified Manning equation (overland flow)
$$v = \frac{\left(R\sqrt{s}\right)}{n} \qquad (2)$$

Discharge
$$Q = Av \qquad (3)$$

Discharge data were then combined with sample concentration data to calculate P and SS fluxes:

Flux (instantaneous load)
$$F = cQ \qquad (4)$$

where: $v =$ Velocity (m s^{-1})

$R =$ Hydraulic radius (m)

$s =$ Slope gradient (m m^{-1})

$n =$ Manning’s n

$A =$ Area (m^2)

$c =$ Concentration (µg l^{-1})

The Manning equation was selected for estimation of flow discharge, as it meant that a single depth measurement could be taken and combined with the flow pathway profile and slope information to give an estimate of discharge. Discharge could then be combined with the concentration data to allow calculation of P and SS fluxes. Other methods of discharge measurement such as salt dilution gauging and the use of stage monitoring were considered, but were deemed either too costly, too time consuming, or inappropriate for logistical reasons.

A Manning's n value of 0.03 was selected for the stream using Cowan's (1956) Method (c.f. Dingman, 1984). This value represents a clean straight channel at full stage with no riffles or pools. An n value of 0.4 for the tracks was selected, which is the highest overland flow value reported by Dingman (1984). The surfaces of the farm tracks did not approximate to any of the overland flow surfaces reported, and this value was therefore chosen to represent the high track roughness caused by wheeling patterns and debris. A modified form of the Manning equation was used for overland flow velocity estimations (Equation 2), as mixed flow conditions are likely to operate in this flow type, where eddies due to raindrop impacts or boundary irregularities are large relative to the shallow depth of flow.

Data were analysed using summary statistics, and relationships between variables were explored through regression analysis using Excel and Minitab. Analysis involved assessment of spatial and temporal patterns in flow concentration and flux data, downstream and downtrack variations, and consideration of the importance of overland flow and drain inputs to the stream by comparison of fluxes.

Results

Pre-Event Survey

Two visits in November 2003 and January 2004 were used to carry out the pre-event survey. Tracks A, B and C and field drains X, Y and Z were identified as important connectivity pathways linking the hillslope to the stream (Figure 1). Thirteen stream monitoring points (S1 to S13) were selected for the 120 m channel reach, located at approximately 12 m intervals. The profiles for stream monitoring locations and drain outlets were carried out using 10 m horizontal intervals, and the depth of each location was then measured.

Event Monitoring

Representativeness of Event

The site was monitored during a rainfall event of 11 mm on 19th March 2004. Rainfall was not continuous and involved several heavier rainfall periods over a seven hour duration (Figure 2). The event monitored ranked seventeenth in terms of magnitude (total rainfall) out of sixty-four events for the winter sampling season, ranging between 0.8 and 38 mm in total. Of the events recorded in the winter sampling season, 22nd October 2003 to 14th April 2004, four of the events recorded were between 10 and 12 mm in total, while the mean event size was 8.8 mm. This event is likely to represent transfers in commonly occurring events.

Selection of Overland Flow Monitoring Locations

Infiltration-excess overland flow was observed on tracks A, B and C after approximately 5 mm of rainfall, and six runoff monitoring points were selected at the following overland flow (OF) locations: where two pathways converged (OF D), where overland flow entered the stream (OF A, OF E and OF F), and at approximately 10 m intervals down-track (OF B and OF C). Overland flow was also observed on track D but this pathway did not connect to the stream and was not monitored. Saturation-excess overland flow was only observed at the base of field C, and this pathway was monitored at OF G where flow connected with the stream (Figure 1). Flow at OF G did not occur until after the rain had stopped. No flow was observed in this event in field C which contained the runoff plots.

Water Sampling and Depth Measurement

Repeated water sampling and depth monitoring took place downstream, in five sampling rounds (I,II,III,IV,V), with overland flow and drain inputs sampled consecutively where they occurred in the stream sequence (Figure 1). As resource constraints meant it was not possible to monitor all locations simultaneously, or to monitor at the same rate as streamflow, each sample was taken to be representative of the portion of the hydrograph in which it was collected (Figure 2). Each sampling round took between 60 and 85 minutes, depending on the number of locations to be sampled – hence the time delay between stream locations 1 and 13 was up to 85 minutes. Vertical depth of tracks from the horizontal was measured, using a specially designed tool incorporating a ruler and level, at the deepest point on the profile, and runoff samples were collected from the deepest part of the flow using a rinsed beaker. The time delay in samples taken between the up-track and down-track samples ranged between 12 and 14 minutes for a distance of approximately 50 m. Collection of a 100 ml sample took less than one minute even at the lowest discharge rate recorded on the track. At the lowest runoff velocity, it was calculated that runoff would take up to 8 minutes to flow between sampling locations. The results for discharge, SS and P are described below by flow pathway.

Overland Flow

High temporal and spatial variability was present in the concentration data for the observed track overland flow locations (Figure 4). Mean discharges were highest at locations OF A and OF E where overland flow entered the stream (Table 1). Mean SS concentration was 466 mg l^{-1}, but was considerably higher than this at OF A. Mean TP concentration for all overland flow samples was 1566 µg l^{-1}, but was again much higher at OF A, where this was associated with the $TP_{>0.45\mu m}$ phase. In contrast, high TP concentrations at OF B closest to the hardstanding were related to higher than average $TP_{<0.45\mu m}$ concentrations. Total P fluxes were highest at OF A and OF E. Differences in concentrations between infiltration-excess overland flow from the tracks and saturation-excess overland flow from the field were also found to exist, with lower P (426 and 341 µg l^{-1}) and SS (104 and 68 mg l^{-1}) concentrations for the field, and with $TP_{<0.45\mu m}$ contributing a much greater proportion of P to TP than flow from the tracks (79 % compared to 36 %).

Drainflow

Mean drainflow discharges were estimated as 4.5, 8.4 and 156 l s^{-1} for drain X, drain Y and drain Z respectively (Table 1, Figure 4). Discharge from drain Y from the hardstanding remained constant over the sampling period, but discharge in drains X and Z peaked at time IV on the falling limb of the hydrograph (Figure 2). Suspended sediment concentrations were highest in drain X, but the highest TP and $TP_{>0.45\mu m}$ concentrations were in drain Y from the hardstanding. Total P fluxes in drains X and Y were below 13 mg s^{-1}, but fluxes in drain Z were much higher, peaking at time III at 190 mg s^{-1}.

Streamflow

Data varied both spatially over the monitored stream reach and temporally over the event (Figure 5). Estimated discharge did not increase as expected downstream, but varied between sampling locations (Table 1). However, as the same discharge pattern was seen at baseflow, this may be due to bed seepage from the artificial channel. The lag time from the start of rainfall to peak discharge was approximately 8 hours, with a peak lag time of approximately 4 hours (Figure 2). Mean TP and SS concentrations increased downstream, in association with the $TP_{>0.45\mu m}$ phase, while the $TP_{<0.45\mu m}$ fraction remained similar throughout the reach. The complex downstream discharge pattern resulted in complex patterns of downstream fluxes of TP. At time III, TP and SS fluxes increased throughout the reach, however, at all other times overall fluxes decreased throughout the reach. In streamflow, TP was initially dominated by $TP_{>0.45\mu m}$, but the $TP_{<0.45\mu m}$ phase became increasingly important during the event, until it constituted the greatest proportion of TP by time V on the falling limb of the hydrograph. In both streamflow and drainflow, strong relationships existed between TP and $TP_{<0.45\mu m}$ (streamflow: $r^2 = 0.82$, drainflow: $r^2 = 0.88$), but the $TP_{<0.45\mu m}$ phase was considerably less important in overland flow, with strong relationships between TP and $TP_{>0.45\mu m}$ ($r^2 = 0.73$) and $TP_{>0.45\mu m}$ and SS ($r^2 = 0.92$). All relationships are significant at $p < 0.05$.

Comparison of Flow Pathways

The use of P and SS fluxes has allowed comparison of P and SS transfers in different pathways over space and time, and hence the influence of different P and SS pathways and inputs to the stream to be evaluated (Table 1). The TP concentrations recorded in overland flow from the hardstanding at Location B are high (mean 2283 μg l^{-1}), but the fluxes at this location were low in comparison to the other overland flow locations, especially when compared to the drain inputs. Estimates of total event P fluxes for different pathways suggest that drainflow inputs from drain Z in field C (the grass field across the stream from the hardstanding) dominated the inputs, although the other drains were also important contributors of P and sediment to the stream reach. In comparison to the drain inputs, overland flow P inputs from the tracks to the stream were very low. At several stream locations, estimated flux overland flow and drain inputs could not account for the differences in P or SS fluxes between reaches, while the TP flux differences between stream locations S11 and S12 are much smaller than the TP flux inputs from drain Z, which flows into the stream in this reach.

Representativeness of results

Comparison of the results of this field trial to data for similar sites allows some assessment of the representativeness of the results. The in-field concentrations recorded in this study (341 and 426 μg l^{-1}) are at the lower end of the range reported from the Smisby, Leicestershire, grassland catchment (213-2483 μg l^{-1}) (Dils and Heathwaite, 1996;2000; Heathwaite and Dils, 2000). The track concentrations are higher (788-3708 μg l^{-1} for TP, 181-2106 μg l^{-1} for $TP_{<0.45\mu m}$), but can be considered within the context of the overland flow data reported from point sources by Dils and Heathwaite (1996) (TP concentrations: 2210-3420 μg l^{-1}, $TP_{<0.45\mu m}$ concentrations: 1870-3410 μg l^{-1}). The larger range of the East Knoyle track data may reflect the effect of downslope sampling producing a reduction in concentrations with distance from the hardstanding source. For broader context, an extensive overland flow dataset sampled between 1989 and 1998 in arable field plots at Woburn under a range of crop types found average TP concentrations of 1220 μg l^{-1}, with a maximum of 7700 μg l^{-1} and a minimum of 90 μg l^{-1} (Quinton, pers. comm.).

For drainflow, TP concentrations from the three East Knoyle drains (258-1557 $\mu g\ l^{-1}$) fit well within the range found in arable drainage at Rosemaund, Herefordshire (750 to 1200 $\mu g\ l^{-1}$) (Chapman et al., 2001), and in grassland drainage at Smisby (233-966 $\mu g\ l^{-1}$), Rowden, Devon (132 $\mu g\ l^{-1}$) and Rosemaund (220-1800 $\mu g\ l^{-1}$) (Dils and Heathwaite, 1999; Haygarth et al., 1998; Withers and Lord, 2002). In streamflow, concentrations ranged between 211 and 657 $\mu g\ l^{-1}$ for TP, 96 and 525 $\mu g\ l^{-1}$ for $TP_{<0.45\mu m}$, and 26-125 $mg\ l^{-1}$ for SS. Mean values reported by Jarvie et al. (2005a) for the Sem, of which the East Knoyle stream is a tributary, are 212 $\mu g\ l^{-1}$ for TRP (the molybdate reactive portion of TP) and 23 $mg\ l^{-1}$ for SS.

Post-Event Survey

At the end of the storm, the post-event survey was carried out. Overland flow locations identified during the event were profiled using horizontal intervals of 5 cm, and slope measurements were taken. Residual sediment was present at each of the six track overland flow locations, and this was also sampled. Results of sediment sampling data are shown in Table 2. Comparison of sediment and overland flow characteristics shows that mean track overland flow TP concentrations are strongly related to the proportion of clay ($r = 0.82$, $p<0.05$) particles in the residual sediment. Mean track overland flow TP concentrations are also related to Sediment TP concentrations ($r = 0.72$), although this relationship is not significant at $p<0.05$. Mean water $TP_{<0.45\mu m}$ concentrations are very strongly related to mean water SS concentrations in overland flow from the tracks ($r = 0.98$, $p<0.01$). Although only a limited number of samples were collected in this study, the results suggest that there is potential for using the characteristics of post-event sampled sediment to understand event P transfers.

Discussion

The application of this methodology, through promoting observation of processes and allowing quantification and comparison of pathways, has allowed assessment of P transfer dynamics at East Knoyle. The results have shown that inputs of P to the stream reach studied were dominated by just one field drain. Despite the farm track connecting the hardstanding, a potential P source, directly to the stream, comparison of fluxes has shown this track was of less importance in P transfer and delivery than each of the three field drains. No overland flow was observed on the field with runoff plots in this event, although the volume of runoff across this field in the 2003-2004 hydrological year was reduced by subsoiling (Withers *et al.*, In press). Where in-field overland flow did occur, it appeared to be generated by saturation-excess overland flow after rainfall had ended, and although directly connected to the stream, this pathway was of little significance in P transfer. Field observation at this site suggests, therefore, that P transfer in overland flow in agricultural catchments may be particularly associated with infiltration-excess flows generated on hard surfaces such as farm tracks heavily compacted by machinery and livestock. Observations on the tracks showed that overland flow generation from these surfaces is dependent on rainfall supply and on the process of ponding and initiation of downslope flow, which is controlled locally due to the roughness of the track surface. As flow is likely to occur on hard surfaces even in small events, it is suggested that this methodology may be appropriate for application to all sizes of events.

Calculations of SS and P fluxes at different times throughout the event have allowed the transfer of SS and P to be compared both spatially and temporally. This research has helped to highlight the complexity of the inter-event transfers in each of the flow pathways, demonstrating that processes, concentrations and fluxes change both spatially and temporally over an event. Where high temporal and spatial variability in overland flow has been observed elsewhere, it has been thought to reflect the nature of variable rainfall conditions on flow pathways and sediment and P transport (Heathwaite and Dils, 2000). However, the results also suggest that storage and sediment-P interactions are likely to have operated in-track. The variability in streamflow data described in Section 5.2.6 is likely to be due to a combination of factors, which could include instream processes such as channel bed transmission losses, subsurface flow inputs, and sediment and P release or recycling from bed storage (e.g. Jarvie *et al.*, 2005b).

The methodology applied at East Knoyle highlights two main challenges. The first is that measurements of discharge across land surfaces and in streams with no permanent monitoring structures are problematic. Use of the Manning's method to calculate discharge introduces the greatest degree of uncertainty involved in the method, as calculated discharges, and hence the P and SS fluxes, were estimates. This challenge could in part be addressed through the installation of a permanent monitoring infrastructure of weirs and stage recorders, which would allow accurate discharge measurements to be monitored, although one of the advantages of the methodology in its current form is that it can be applied to a catchment with no existing monitoring infrastructure. The uncertainty in point discharge measurements could also be reduced through the use of a combination of discharge measurements, including salt dilution and float methods, and calibration of these to stage measurements for each monitoring location. For the temporary flow pathways, where permanent infrastructure is inappropriate, the design and use of temporary sampling devices which direct flow through a particular monitoring location would allow discharge measurements to be taken manually, and also enable easier sample collection at overland flow locations.

The second challenge relates to contemporaneous spatial sampling of events. It was not possible to collect samples at a large number of locations at the same time for the results reported here, and this has two implications. It introduces uncertainty in the P comparisons between scales and times of observation, and means that upslope sampling may have affected P transfer in overland flow pathways. The uncertainty in data for comparisons could be reduced through the use of automated samplers which would allow simultaneous sampling of continuous flow pathways, and also free up resources for point sampling at other locations, allowing increased temporal resolution of point sampling to produce more constrained data. Where automated sampling is impractical, for example in temporary flow pathways, the issue of non-simultaneous upslope sampling may be unavoidable. In this study, as the flow pathway was not blocked by sample collection and the collection time was minimal in comparison to the flow rate and sampling interval (see Section 5.2.3), it can be argued that that the volume of runoff removed was unlikely to alter the effectiveness of the pathway with regard to flow dynamics and hence P transfer.

Conclusions

Further progress in model development is inhibited by limited process understanding and data on the quantification of P transfer and delivery, and new monitoring tools are needed which will provide a framework for collection of P transfer and delivery data at a range of scales in agricultural catchments. A field methodology incorporating the techniques of event-based, on-site observation and sampling of P within a flexible, non-plot based structure has been described and applied to a first order stream catchment in the Hampshire Avon. The results show that P transfers to the stream were dominated by inputs from one field drain, and that overland flow inputs, despite being directly connected to the stream and containing higher P concentrations than drainflow, were of less overall significance. Furthermore, the results have shown that the processes of P transfer and delivery to the stream are particularly complex, changing both spatially and temporally over an event.

The field methodology described has been designed as a research tool to further understand P delivery in small agricultural catchments, and compliments traditional monitoring techniques. The use of three phases of field monitoring allows the site to be considered in relation to pre-event, event, and post-event dynamics. For the methodology to be useful, it needs to be applied to a variety of catchments with varying land use, soil and climate, for a variety of event sizes and rainfall intensities. The simplicity and flexibility of the method, and the fact that it has been demonstrated in a catchment with no permanent monitoring infrastructure, demonstrates that this methodology can be easily applied elsewhere. Even taking into account the degree of uncertainty inherent in the method, the data provided by this method are valuable, as they have allowed the event based P dynamics of a previously unmonitored site to be quantified. The results presented in this study suggest that the application of the methodology to other sites would be of benefit in furthering our understanding of P transfer and delivery in small agricultural catchments.

Acknowledgements

This research was carried out as part of a studentship funded by an EPSRC Doctoral Training Award to Clare Deasy. It includes work undertaken as part of the PSYCHIC project PE0202, funded by the Department for the Environment, Food and Rural Affairs, the Environment Agency and English Nature to Louise Heathwaite. We wish to thank Paul Withers and Adam Bates at ADAS for site access and background data, John Quinton at Lancaster for allowing the use of previously unpublished contextual data from Woburn, Graham Allsopp at Sheffield for his help in producing the figures, and Jon Bridge and Lucy Bolton for invaluable field and lab assistance.

References

Beven, K., Heathwaite, L., Haygarth, P., Walling, D., Brazier, R. and Withers, P., 2005. On the concept of delivery of sediment and nutrients to stream channels. Hydrological Processes, 19(2): 551-556.

Chapman, A.S., Foster, I.D.L., Lees, J.A., Hodgkinson, R.A. and Jackson, R.H., 2001. Particulate phosphorus transport by sub-surface drainage from agricultural land in the UK. Environmental significance at the catchment and national scale. The Science of the Total Environment, 266: 95-102.

Dils, R.M. and Heathwaite, A.L., 1996. Phosphorus fractionation in hillslope hydrological pathways contributing to agricultural runoff. In: M.G. Anderson and S.M. Brookes (Editors), Advances in Hillslope Processes. Wiley, Chichester, pp. 229-251.

Dils, R.M. and Heathwaite, A.L., 1999. The controversial role of tile drainage in phosphorus export from agricultural land. Water Science and Technology, 39(12): 55-61.

Dils, R.M. and Heathwaite, A.L., 2000. Tracing phosphorus movement in agricultural soils. In: I.D.L. Foster (Editor), Tracers in Geomorphology. Wiley, Chichester, pp. 259-276.

Dingman, S.L., 1984. Fluvial Hydrology. Freeman, New York.

EA, 2002. LANDCARE Baseline Monitoring Report. Environment Agency (South Wessex Area), pp. 70.

Gburek, W.J., Sharpley, A.N. and Pionke, H.B., 1996. Identification of critical source areas for phosphorus export from agricultural catchments. In: M.G. Anderson and S.M. Brookes (Editors), Advances in Hillslope Processes. Wiley, Chichester, pp. 263-282.

Harris, G. and Heathwaite, A.L., 2005. Inadmissible evidence: knowledge and prediction in land and riverscapes. Journal of Hydrology, 304(1-4): 3-19.

Haygarth, P.M., Hepworth, L. and Jarvis, S.C., 1998. Forms of phosphorus transfer in hydrological pathways from soil under grazed grassland. European Journal of Soil Science, 49: 65-72.

Haygarth, P.M., Wood, F.L., Heathwaite, A.L. and Butler, P.J., 2005. Phosphorus dynamics observed through increasing scales in a nested headwater-to-river channel study. Science of The Total Environment, 344(1-3): 83-106.

Heathwaite, A.L. and Dils, R.M., 2000. Characterising phosphorus loss in surface and subsurface hydrological pathways. The Science of the Total Environment, 251-252: 523-538.

Heathwaite, A.L., Dils, R.M., Liu, S., Carvalho, L., Brazier, R.E., Pope, L., Hughes, M., Phillips, G. and May, L., 2005. A tiered risk-based approach for predicting diffuse and point source phosphorus losses in agricultural areas. Science of The Total Environment, 344(1-3): 225-239.

Jarvie, H.P., Neal, C., Withers, P.J.A., Wescott, C. and Acornley, R.A., 2005a. Nutrient hydrochemistry for a groundwater-dominated patchment: The Hampshire Avon, UK. Science of the Total Environment, 344(1-3): 143-158.

Jarvie, H.P., Jurgens, M.D., Williams, R.J., Neal, C., Davies, J.J.L., Barrett, C. and White, J., 2005b. Role of river bed sediments as sources and sinks of phosphorus across two major eutrophic UK river basins: the Hampshire Avon and Herefordshire Wye. Journal of Hydrology, 304(1-4): 51-74.

Jordan, P., Arnscheidt, J., McGrogan, H. and McCormick, S., 2005. High-resolution phosphorus transfers at the catchment scale: the hidden importance of non-storm transfers. Hydrology and Earth System Sciences, 9(6): 685-691.

Kleinman, P.J.A., Srinivasan, M.S., Dell, C.J., Schmidt, J.P., Sharpley, A.N. and Bryant, R.B., 2006. Role of rainfall intensity and hydrology in nutrient transport via surface runoff. Journal of Environmental Quality, 35(4): 1248-1259.

Kronvang, B., Grant, R., Laubel, A.R. and Pedersen, M.L., 2002. Quantifying sediment and nutrient pathways within Danish agricultural catchments. In: P.M. Haygarth and S.C. Jarvis (Editors), Agriculture, Hydrology and Water Quality. CAB International, Wallingford, pp. 281-301.

McDowell, R.W., Sharpley, A.N. and Folmar, G.J., 2001. Phosphorus export from an agricultural watershed: Linking source and transport mechanisms. Journal of Environmental Quality, 30: 1587-1595.

Murphy, J. and Riley, J.P., 1962. A modified single solution method for the determination of phosphate in natural waters. Analytica Chimica Acta, 27: 31-36.

Pionke, H.B., Gburek, W.J., Sharpley, A.N. and Schnabel, R.R., 1996. Flow and nutrient export patterns for an agricultural hill-land watershed. Water Resources Research, 32(6): 1795-1804.

Wainwright, J., Parsons, A.J. and Abrahams, A.D., 2000. Plot-scale studies of vegetation, overland flow and erosion interactions: case studies from Arizona and New Mexico. Hydrological Processes, 14(16-17): 2921-2943.

Withers, P.J., Hodgkinson, R.A., Bates, A. and Withers, C.L., In press. Soil cultivation effects on sediment and phosphorus mobilization in surface runoff from three contrasting soil types in England. Soil & Tillage Research.

Withers, P.J.A. and Lord, E.I., 2002. Agricultural nutrient inputs to rivers and groundwaters in the UK: policy, environmental management and research needs. The Science of the Total Environment, 282-283: 9-24.

Wood, F.L., Heathwaite, A.L. and Haygarth, P.M., 2005. Evaluating diffuse and point phosphorus contributions to river transfers at different scales in the Taw catchment, Devon, UK. Journal of Hydrology, 304(1-4): 118-138.