Environmental RTDI Programme 2000–2006

EUTROPHICATION FROM AGRICULTURAL SOURCES – Phosphorus Concentration and Flow (2000-LS-2.1.1b)

Final Report

Prepared for the Environmental Protection Agency

by

Teagasc, Johnstown Castle, Wexford

Authors:

Donnacha Doody, Richard Moles, Hubert Tunney and Isabelle Kurz

ENVIRONMENTAL PROTECTION AGENCY

An Ghníomhaireacht um Chaomhnú Comhshaoil
PO Box 3000, Johnstown Castle, Co. Wexford, Ireland

Telephone: +353 53 60600 Fax: +353 53 60699
E-mail: info@epa.ie Website: www.epa.ie

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Details of Project Partners

Donnacha Doody
Department of Chemical and Environmental Sciences
Lonsdale Building
Unversity of Limerick
Limerick
Ireland

Tel.: +353 61 213013
E-mail: donnacha.doody@ul.ie

Richard Moles
Department of Chemical and Environmental Sciences
Lonsdale Building
University of Limerick
Limerick
Ireland

E-mail: richard.moles@ul.ie

Hubert Tunney (Project Leader)
Teagasc
Johnstown Castle Research Centre
Co. Wexford
Ireland

E-mail: htunney@johnstown.teagasc.ie

Isabelle Kurz
Teagasc
Johnstown Castle Research Centre
Co. Wexford
Ireland

E-mail: ikurz@johnstown.teagasc.ie

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1 Introduction

Water quality in Ireland continues to deteriorate despite attempts to minimise the impact of pollution on lakes and rivers (Lucey *et al.*, 1999; EPA, 2004). The cause of this decline has in a large part been attributed to nutrient enrichment of lakes and rivers from agricultural sources (EPA, 2004). Phosphorus (P) is often the limiting nutrient within aquatic freshwater ecosystems, and so increased inputs from agricultural sources can result in eutrophication (Foy *et al.*, 1995; Jeffrey, 1998; Tunney *et al.*, 1998; EPA, 2004).

Licensing of point sources of pollution from wastewater treatment plants has resulted in a decline in P inputs to lakes and rivers, although in many cases there has been no noticeable improvement in water quality (Foy *et al.*, 1995; EPA, 2004). Diffuse sources of P from agricultural catchments are much more difficult to control and hence much attention now focuses on the control of P inputs from these sources. Phosphorus loss from diffuse sources results from a complex interaction between catchment soils, hydrology, and land management (Haygarth and Jarvis, 1999).

While environmentally significant concentrations of P have been reported in subsurface flow (Heckrath *et al.*, 1995; Sims *et al.*, 1998), overland flow is considered to be the main pathway of P loss from agricultural grassland soils (Sharpley *et al.*, 1994). Phosphorus in overland flow may be lost in particulate or dissolved forms, with total dissolved P (TDP) being the major fraction exported from grasslands (Sharpley *et al.*, 1994; Nash *et al.*, 2000; Pionke *et al.*, 2000). A clear relationship between soil test P (STP) concentrations and P concentration in overland flow has been demonstrated in a number of studies (Sharpley *et al.*, 1994; Sharpley, 1995; Pote *et al.*, 1999a; Kurz, 2002; Tunney, 2002). Pautler and Sims (2000) demonstrated a near–linear increase in soluble P, easily desorbable P and total sorbed P with an increase in STP. Increasing STP above agronomical optimum values increases the risk of P loss to water due to the increasing degree of P saturation (DPS) (Pautler and Sims, 2000).

1.1 Objective

A number of authors have demonstrated the existence of a distinctive relationship between dissolved P concentration in overland flow and overland flow rate (Stamm, 1997; Pote et al., 1999a; Heathwaite and Dils, 2000; Tunney *et al.*, 2000; Kurz, 2002). As overland flow rate increases, there is a corresponding increase in dissolved reactive P (DRP) concentration in overland flow (Fig. 1.1). This is counter-intuitive as dilution would be expected to decrease the P concentration.

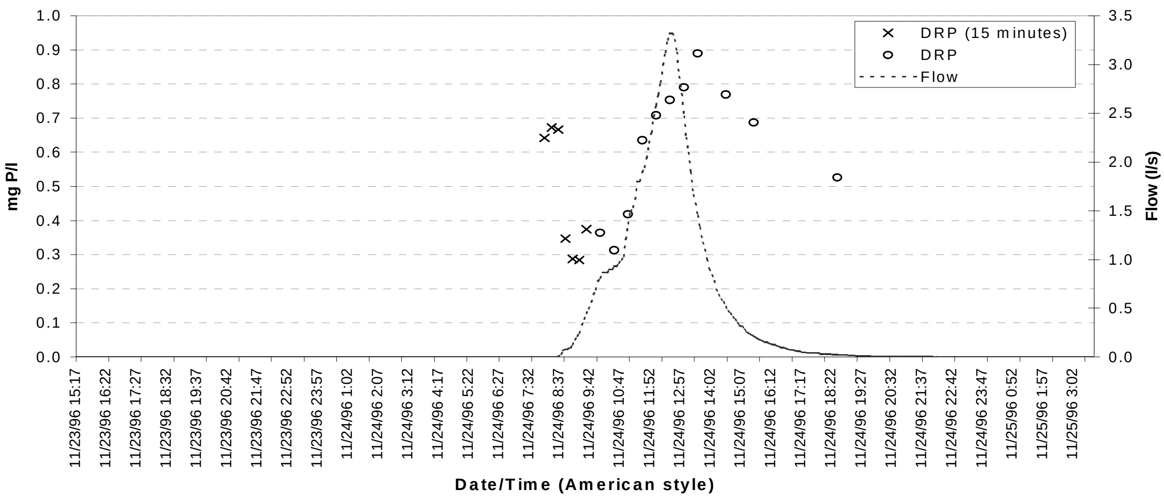

Figure 1.1. Increase in dissolved reactive P (DRP) concentration with an increase in overland flow rate (Kurz, 2002).

Investigations have established the key processes that result in the movement of P from soil to water. However, the mechanisms controlling the rise in dissolved P concentration with an increase in overland flow rate have not been identified. Hence, the objective of this project is to investigate those processes controlling P loss in overland flow, so as to identify, describe and evaluate mechanisms responsible for this observed increase in dissolved P concentration with an increase in overland flow rate. This report is based on work for a Ph.D. thesis where more detailed information is presented (Doody, 2004).

To investigate all the possible controls on the increase in P concentration with an increase in overland flow rate is beyond the scope of this study. On the basis of the literature review, a number of physico–chemical, soil, hydrological and soil/water interface processes were identified and hypotheses were then developed in order to evaluate the significance of these mechanisms through experimental methods.

1.2 Hypotheses

1.2.1 Physico–chemical processes

Desorption was identified as a key process in the loss of dissolved P from soil to water. It acts as a link between the sources of P in the soil and the transport vectors provided by the site hydrology. Desorption has been investigated in depth by numerous authors (Pautler and Sims, 2000; Maguire et al., 2001; McDowell and Sharpley, 2001; Vadas and Sims, 2002). No work was found in the literature that investigated the impact of flow rate on P desorption from soil.

Hypothesis 1: An increase in flow rate results in an increase in dissolved P desorption from soil.

1.2.2 Soil processes

Soil test P and soil drying/re-wetting may also play a role in the increase in P concentration with an increase in overland flow rate. In small-scale studies, drying and re-wetting of soil results in an increase in P loss from the soil (Sharpley, 1980; Turner and Haygarth, 2001). The potential impact of soil drying cycles on P loss in overland flow has also been demonstrated by Pote *et al.* (1999b) and Kurz (2002). A strong correlation between STP and P concentrations in overland flow has been reported by a number of authors (Sharpley et al., 1994; Sharpley, 1995; Pote *et al.*, 1999a; Kurz, 2002; Tunney, 2002).

Hypothesis 2: Variations in soil test P have an impact on the relationship between dissolved P concentration and overland flow rate.

Hypothesis 3: Soil drying/re-wetting cycles have an impact on the relationship between dissolved P concentration and overland flow rate.

1.2.3 Transport processes

Saturation excess overland flow is the dominant type of overland flow generated under Irish conditions (Diamond and Sills, 2001). It originates in areas referred to as variable source areas (VSAs) (Gburek and Sharpley, 1998). These areas rapidly expand and contract during rainfall events (Pionke *et al.*, 1988; Gburek and Sharpley, 1998). This expansion results in an increase in the area of saturation and in an increase in the length of the flow path over which overland flow travels. With this increase, the volume of overland flow increases.

Hypothesis 4: An increase in the flow path length of overland flow results in an increase in dissolved P concentration in overland flow

Hypothesis 5: An increase in overland flow rate results in an increase in dissolved P concentration in overland flow.

1.2.4 Soil/water interface processes

Mixing is considered to be the key mobilisation process occurring at the soil/water interface in grassland soil. Although erosion processes in grasslands are diminished due to the presence of the grass sward (Prosser et al., 1995; Carroll and Tucker, 2000), grass filter strip studies have demonstrated that particulate P (PP) may still be mobilised over short distances (Magette *et al.*, 1989; Abu-Zreig *et al.*, 2003). Significant quantities of dissolved P may desorb from particles entrained in overland flow due to the selective erosion of clay-sized particles (Quinton *et al.*, 2001). The relative contribution of this to edge-of-field losses has not been reported.

Hypothesis 6: Particulate P is mobilised over short distances within grasslands.

Hypothesis 7: Dissolved P, desorbed from soil particles entrained in overland flow, makes a significant contribution to the dissolved P edge-of-field losses.

2 Materials and Methods

2.1 Introduction

Three experimental methods were developed to investigate the seven hypotheses outlined above. Dissolved P fractions such as DRP, total reactive P (TRP), and total dissolved P (TDP) were the main P fractions investigated during this study. However, where possible, the total P (TP) and particulate P (PP) and dissolved organic P (DOP) fractions were all recorded and their role in the increase in dissolved P concentration with flow was discussed.

Experiment 1: Continuous flow methods were used to investigate the impact of flow on dissolved P concentration in drainage from columns of soil. The impact of drying and wetting of soil on the quantity and forms of P (TP, TDP, TRP, DRP, DOP) in the drainage from the soil columns was also investigated.

Experiment 2: A laboratory flume was constructed to investigate the impact of overland flow rate, flow path length, and time between overland flow events on P concentration and P forms (TP, TDP, TRP, DRP, PP, DOP) in overland flow.

Experiment 3: A 10 m × 1 m hydrological isolated field site was monitored for overland flow, water quality and soil moisture. The aim was to investigate the impact of variations in soil moisture on P loss and also the in-field mobilisation of PP on the concentration and forms of P (TP, TDP, TRP, DRP, PP, DOP) transported in overland flow.

A complete description of experimental methods is reported in Doody (2004).

2.2 Experiment 1: Continuous Flow Soil Column Experiment

2.2.1 Soil preparation

Soil samples were taken from plots in a long-term, field-scale grazing, soil fertility trial in Johnstown Castle, Co. Wexford, Ireland (Culleton *et al.*, 1999). Three different P fertiliser treatments of 0 kg/ha/year, 15 kg/ha/year and 30 kg/ha/year were applied to plots over a 30-year period.

Soil samples were taken to a depth of 0–200 mm from plots of the three fertiliser treatments. Samples were also taken to a depth of 0–100 mm from the 0 kg/ha plot. This provided soil samples with a range of soil P index levels (Coulter, 2001) from 1–4 (Table 2.1). The samples were taken in areas of similar soil types classed as gleys. The soils were analysed for a range of variables (Table 2.1). They were air dried at 40°C for 16 h and then sieved (2 mm) before storage.

Table 2.1. The characteristics of the soils used in the column and flume experiments from a field-scale long-term fertility trial at Johnstown Castle.

Soil P status	Index 1 (0–3 mg/l)	Index 2 (3.1–6 mg/l)	Index 3 (6.1–10 mg/l)	Index 4 (>10 mg/l)
P treatments (kg/ha/year)	0	0	15	30
Properties				
Sample depth (mm)	0–100	0–20	0–20	0–20
Phosphorus (mg/l) (Morgan's P)	2.8	6.2	9.6	29.8
pH	6.3	5.5	5.9	6.1
Potassium (mg/l)	113	252	160	164
Magnesium (mg/l)	353	357	424	561
Organic matter (%)	11.8	15.8	12.2	18.2
Total iron (mg/kg)	28320	14880	13680	23920
Total aluminium (mg/kg)	25600	13940	11460	22280
Bulk density	0.75	0.67	0.74	0.63

2.2.2 Experimental design

Glass wool was packed into the bottom of chromatography columns (300 mm × 20 mm) to filter out any sediment prior to water sample collection. Columns were then packed with 50 g of the dried soil. The soil was then wetted with deionised water. The columns were weighed after draining overnight to ensure that there were similar volumes of water in the columns prior to the start of the experiment. The level of the soil was marked in each column. A column was replaced if there was a deviation in the soil level from this mark as it was assumed that there would be a corresponding change in bulk density.

New soil was packed into the columns for each experimental run. All equipment was colorimetrically acid washed with 2% H_2SO_4 between runs and rinsed with deionised water.

The percolation solution used was deionised water. A peristaltic pump was used to pump the deionised water through the soil columns at a set flow rate during each experiment. The experiment was carried out over 6 h, with 5-ml samples collected every 15 min for the first 30 min and every 30 min thereafter. The unfiltered samples were analysed within 24 h for TRP using an automatic Konelab 900 analyser, which measures P concentration colorimetrically (Labsystems Group, 2000).

2.2.3 Flow rate

The impact of flow on P desorption was examined at three flow rates: (i) 0.5 ml/min, (ii) 1.0 ml/min, and (iii) 1.5 ml/min. These flow rates were selected because during preliminary runs it was found that at rates above 1.5 ml/min there was a build-up of pressure in the column, which would result in a change in the bulk density of the soil.

2.2.4 Soil drying/re-wetting

To examine the impact on drying/re-wetting on TDP loss from the soil, samples from Index 2, 3 and 4 soils were subdivided, with one part dried at 40°C for 16 h, while the other subsample remained wet and was used within hours of being sampled. Continuous flow experiments were carried out on all the subsamples as per previous methods outlined above. However, only one flow rate of 1 ml/min was used during this experiment.

To limit the impact of the time interval prior to sample analysis, samples of leachate from the drying/re-wetting experiments were mixed with potassium persulphate digest and then digested in an autoclave at 121°C for 30 min. The digests were analysed on a Burkard segmented flow autoanalyser which measures P colorimetrically (Murphy and Riley, 1962) for TDP and not TRP as in previous experiments.

2.2.5 26-Hour experiment

A 26-hour experimental run was carried out on re-wetted Index 1, 2, 3, and 4 soils, as outlined above, to investigate the change in P concentration with a longer time frame than used in the previous experiments. A flow rate of 1 ml/min was used. Samples were collected very 30 min for the first 9 h. The experiment was continued overnight (12 h) and more samples were collected in the morning every 30 min for a further 3 h. Samples were analysed as previously described for TRP

2.2.6 Phosphorus fractions experiment

In order to obtain sufficient sample for P (TP, TDP, TRP, DRP, PP, DOP) fraction analysis, a composite sample was taken over each 30-min period. This experiment was carried out on re-wetted soils from Index 1 to 4 as described above. The composite samples taken over 30 min were subdivided with one half being filtered through 0.4-µm Millipore filter paper and the other remaining unfiltered. A 5-ml subsample from both the filtered and unfiltered samples was mixed with 5 ml potassium persulphate digest and then digested in an autoclave at 121°C for 30 min. A Burkard segmented flow autoanalyser was used to assay all samples for TP and TDP.

A further 5 ml of both samples were stored at 4°C and analysed within 24 h for TRP and DRP using the Konelab 900 colorimetric analyser (Murphy and Riley, 1962). This experiment was carried out for 6 h at a flow rate of 1 ml/min.

2.2.7 Experimental replication

Subsamples of the same soil were run on three separate occasions at a flow rate of 1 ml/min to test the reproducibility of the methods. This was conducted with three subsamples for each of the four STP levels.

2.2.8 Data analysis

The observed temporal patterns of the TRP concentration (P_t) for each of the steady flow columns were empirically described by the following compound equation. It consists of an exponential equation (decreasing) and a lognormal distribution, respectively:

$$[P_t] = [P_0] \cdot e^{-c_1 \cdot t} + \frac{P_d}{F} \cdot N[\ln(t), m, s] \qquad \text{Eqn 1}$$

where t is time (min), $[P_t]$ is the P concentration at time t (mg/l), $[P_0]$ is the P concentration at time 0 (mg/l), c is the treatment-specific parameter (per min), P_d is the total load of desorbable P (mg), F is the flow rate (l/min), N[ln(t),m,s] is the lognormal distribution of the freely available P with time where m is the ln(time of max. P desorption) (min) and s is the ln(standard deviation) (min).

The values of the parameters in the equation were calibrated by minimising the residual sum of squares between the observed TRP concentrations and the concentrations predicted by Eqn 1 for each column. Identical values of P_d were calibrated for columns with identical soil P indices, since P_d is not dependent on flow rate. In addition, for each column, the maximum TRP concentration was calculated as $P(t = e^m)$. The maximum rate of increase of the TRP concentration was found by (i) double differentiation of Eqn 1 with time, (ii) finding the time at which the maximum increase occurred (t_{max}) by solving $d[P_t]/d^2t = 0$, and (iii) calculating the maximum rate of increase as $d[P(t = t_{max})]/dt$.

Subsequently, multiple linear regressions were performed to establish the dependence of the maximum TRP concentrations, the maximum rates of increase of the TRP concentrations, and the model parameters m, s, and P_d (dependent variables) on STP, flow rate and the interaction of STP and flow rate (independent variables).

2.3 Experiment 2: Laboratory Flume

2.3.1 *Laboratory flume*

A galvanised steel laboratory flume was manufactured with the dimensions 3 m × 0.12 m × 0.05 m (Fig. 2.1). At the top end of the flume a 0.8-m long reservoir was constructed and at the end of the flume a funnel-shaped piece of metal was attached at 20 mm depth in the channel. This was to allow for the collection of overland flow from the top 20 mm of the grass sods. The 30 mm below the funnel were left open to allow water not collected as overland flow to exit the flume.

2.3.2 *Soil sampling*

Intact soil sods were taken from the field plots of a long-term field-scale soil fertility grazing trial (see Section 2.2.1) to provide a range of STP levels. The sods were taken intact using a 1 m × 0.15 m steel frame that was driven into the ground to a depth of 60 mm. The frame and intact soil sod were then excavated. The sod was taken in three parts to fill the laboratory flume channel described above. Liquid wax was pumped in between the soil sod and the side of the flume and allowed to solidify to minimise preferential flow between the sides of the flume and the sods.

2.3.3 *Overland flow simulation*

The soil sod was saturated with deionised water and allowed to drain for 16 h before each overland flow simulation experiment was carried out. Two types of overland flow were simulated:

1. Water was pumped into the reservoir at the top of the flume using a four-channel peristaltic pump and allowed to cascade evenly out of the reservoir over

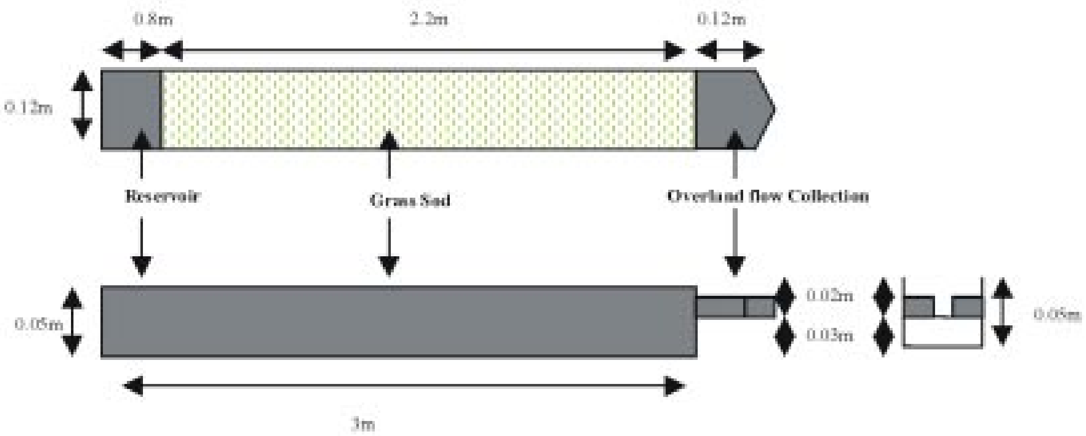

Figure 2.1. Schematic diagram of the flume used in the overland flow simulation experiments.

the sod. The overland flow travelled the length of the flume and samples were collected. This simulated *overland flow from a saturated area* that did not expand during the overland flow event. This was carried out on the Index 3 soil only.

2. The second type was a *variable flow path length* overland flow. A sprinkler system connected to a peristaltic pump was placed at the sod surface to allow the even distribution of water over the sod. The sprinkler was moved up and down the length of the flume using the overhead bar, thereby simulating the expansion or contraction of a VSA during an overland flow event. Three variables were investigated using this method:

   (i) Flow path length

   (ii) Flow rate

   (iii) Time between events.

A number of combinations of flow path lengths were used. Firstly, the expansion of a VSA during a rainfall event was simulated by increasing the length of the flow path. The water source was first placed at 100 mm from the bottom end of the flume. After each 30 min of the 6-h experiments the water source was moved up 200 mm to a total length of 2.2 m. This was carried out on Index 2, 3, and 4 soils.

A second experiment was conducted with increasing and decreasing flow path lengths to investigate the expansion and contraction of a VSA on P (TP, TDP, TRP, DRP, PP, DOP) concentration in overland flow. The water source was first placed 100 mm from the bottom end of the flume and moved up 200 mm every 30 min for the first 3 h, and then decreased 200 mm every 30 min for the remaining 3 h. This was done with a corresponding increase and decrease in flow rate. This was carried out using P Index 2, 3, and 4 soils.

The impact of a corresponding change in flow rate with flow path length was also investigated in a third experiment. Three different flow rates of 44 ml/min (low), 88 ml/min (medium) and 132 ml/min (high) volumes were simulated in combination with a constantly increasing flow path length. This was carried out on Index 2, 3, and 4 soils.

Finally, the impact of time between events was investigated in order to determine the impact of drying/re-wetting on P (TP, TDP, TRP, DRP, PP, DOP) concentration in overland flow. The sod was saturated initially and then left to drain for 16 h. An overland flow simulation was carried out with a steady flow rate of 88 ml/min and constantly increasing flow path length. Following this experiment, the sod was allowed to dry out for 24 h before it was re-saturated and another overland flow simulation carried out. This was repeated for 48-, 96- and 192-h drying periods. This experiment was conducted on the Index 4 soil only.

2.3.4 Sample collection and analysis

During all the experiments, 30-ml overland flow water samples were collected every 30 min for the 6-h duration of each experiment. Samples were analysed as described in Section 2.2.6.

2.3.5 Experimental replication

The same sod of the three soil P index levels was used in each experiment to minimise the effect of spatial variation in STP within a field. However, it was recognised that there may be a gradual decrease in the P (TP, TDP, TRP, DRP, PP, DOP) concentration recorded due to ‘P wash out’ from the soil following multiple overland flow events. This was examined by running an identical experiment (increasing flow path length with a steady flow rate) on the same sod on three occasions and a fourth time on a different sod from the same plot.

Analysis of variance was used to examine if there were any significant differences between the four replications. Multiple linear regressions were carried out to investigate whether flow path length, flow rate, flow velocity, or time between events had a significant impact on P loss in the simulated overland flow.

2.4 Experiment 3: Hydrologically Isolated Field Plot (10 m × 1 m)

2.4.1 Site selection

A site within the Lower Warren Field in Johnstown Castle Estate, Wexford, was selected for the 10 m × 1 m field plot experiment. This site has been monitored for overland flow and water quality since 1997 and there was a historical database available (Kurz, 2002). It was an Index 3 site with an average Morgan’s P value of 8 mg/l. A 10 m × 1 m field plot was hydrologically isolated using 6.2-mm thick stainless steel sheeting in January 2003.

2.4.2 Water sampling and analysis

At the lower end of the field plot, a flume, manufactured from stainless steel, was installed. The flume was placed into the soil at the boundary of the plot and was designed to collect all the overland flow generated within the plot and funnel it into a 30-m wide channel. Water samples were collected using an ISCO automatic sampler (ISCO Inc., 2001). The water samples (75 ml) were collected every 10–15 min, depending on the expected rainfall intensities, until the sampling programme was stopped or 24 samples were collected. Samples were analysed for the P (TP, TDP, TRP, DRP, PP, DOP) using the methods described in Section 2.2.6

2.4.3 Flow measurement

A method was required for flow measurement and triggering of the sampling programme during an overland flow event. The bubbler device attached to the water sampler, which measures flow by measuring changes in pressure due to increasing/decreasing water level, requires at least 30 mm head of water in order to measure flow accurately. A trigger box was designed with a 1 mm × 200 mm slit that acted as a miniature weir. This was placed downslope at the end of the flume channel. Overland flow collected from the plot passed through the flume channel and into the trigger box. The sampling regime was triggered by a change in water level within the box.

2.4.4 Calibration

The trigger box was calibrated in the laboratory prior to installation in the field so that changes in level could be converted to flow using the calibration equation developed.

2.4.5 Field plot instrumentation

Four Time Domain Reflectometer (TDR) probes, which measure the volumetric water content of soil, were installed within the isolated plot to measure changes in soil moisture. These were installed at 2-m intervals down the length of the flume and soil moisture was recorded every 15 min using a CR10X Campbell Scientific data logger. The probes were 300 mm long and so were installed at a 45° angle so as to derive an integrated measurement of soil moisture for the top 150 mm of soil.

Rainfall was measured using a Campbell Scientific tipping bucket rain gauge and automatically recorded every 15 min using a CR10X Campbell Scientific data logger.

3 Results and Discussion

The experiments carried out during this project were at three different scales and investigated different processes involved in P (TP, TDP, TRP, DRP, PP, DOP) loss in overland flow. The experiments were designed to test the hypotheses outlined in Section 1.2. A hypothesis accepted at one scale was then tested at a larger scale. The key results from the three experiments are integrated below and discussed in relation to the increase in P concentration with an increase in overland flow rate. The complete results are presented elsewhere (Doody, 2004).

3.1 Experimental Replication

3.1.1 *Continuous flow column experiment*

The results from the three subsamples of the same Index 2 soil run on three separate occasions at 1 ml/min in the continuous flow experiment are shown in Fig. 3.1. The P (TDP, TRP, DRP) concentrations and trends for all three runs are very similar. Similar results were obtained from the Index 1, 3 and 4 soils (Doody, 2004). ANOVA confirmed that there were no significant differences between runs on soils from the same STP level ($p > 0.05$).

3.1.2 *Laboratory flume experiment*

The results from four different simulated overland flow events with the laboratory flume are summarised in Fig. 3.2. ANOVA was used to examine differences in the means of the four replications for the P (TP, TDP, TRP, DRP, PP, DOP) fractions recorded. No significant differences were found ($p > 0.05$).

3.2 Phosphorus Release Mechanisms

The continuous flow experiment was designed to test the hypothesis that there was an increase in P desorption from soil with an increase in flow rate. Total reactive P loss from the column increased with increasing STP level (Fig. 3.3). The changes in TRP concentration with time for the Index 1 to 4 soils at flow rates of 0.5, 1.0, and 1.5 ml/min are shown in Figs 3.4 to 3.7.

The impact of flow rate and STP on TRP loss from the soil column was analysed using Eqn 1. It accurately described the TRP concentration observed during the continuous flow experiments. For each combination of STP and flow rate, Table 3.1 shows the coefficients of determination between the observed temporal patterns of the TRP concentrations and the patterns described by Eqn 1. The maximum rate of change in TRP concentration was calculated from Eqn 1 and in all cases occurred during Phase 2 (Fig. 3.8) of the continuous flow experiment. The maximum rate of change in TRP concentration was significantly correlated to the STP and to the interaction

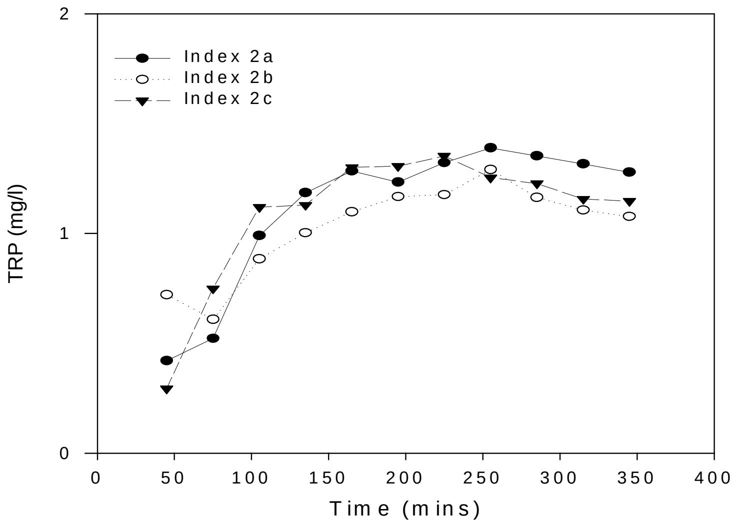

Figure 3.1. Change in total reactive phosphorus (TRP) concentration over time from three subsamples of an Index 2 soil at a 1 ml/min flow rate.

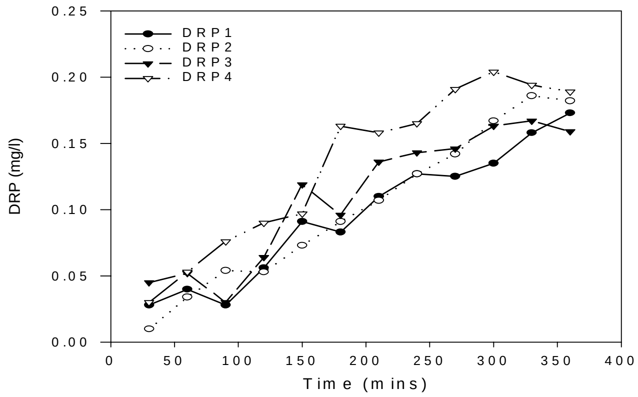

Figure 3.2. Variation in DRP concentration over four overland flow simulation events on grass sods from an Index 4 soil at 88 ml/min flow rate (DRP 1 to 3 was on the same sod and DRP 4 was on another sod (see Section 3.1.2).

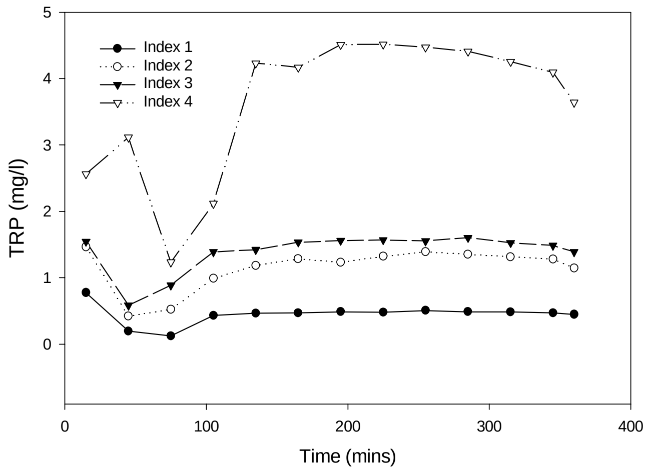

Figure 3.3. Temporal changes in total reactive phosphorus (TRP) concentrations in run-off from Index 1, 2, 3 and 4 soils at a 1 ml/min flow rate.

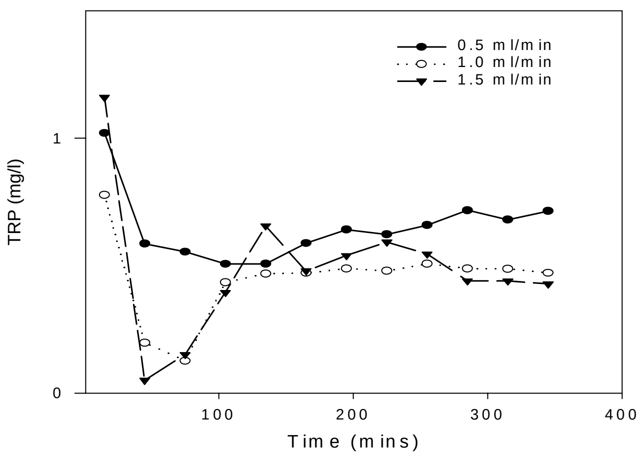

Figure 3.4. Temporal trends in total reactive phosphorus (TRP) concentration in run-off water from an Index 1 soil at three different flow rates.

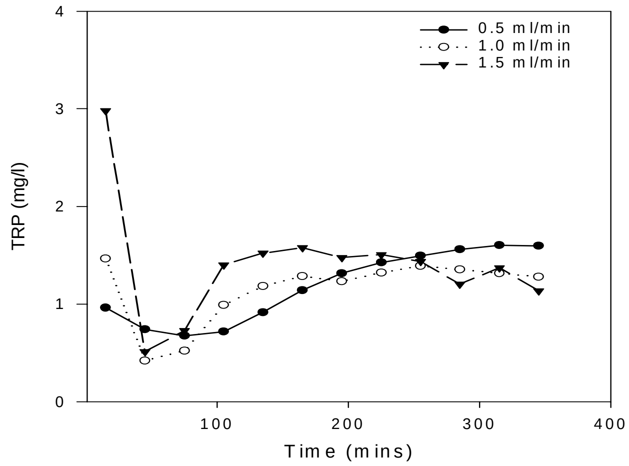

Figure 3.5. Temporal trends in total reactive phosphorus (TRP) concentration in run-off water from an Index 2 soil at three different flow rates.

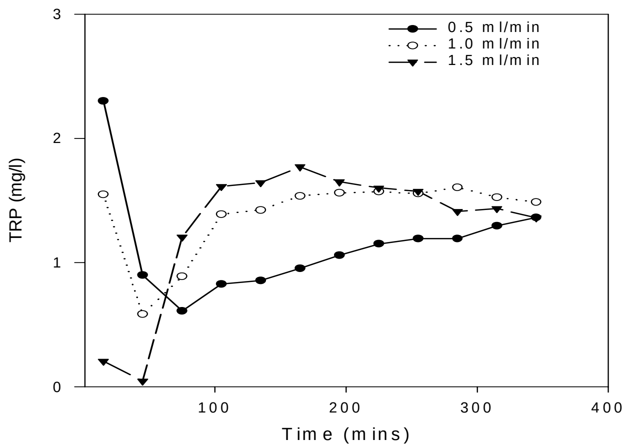

Figure 3.6. Temporal trends in total reactive phosphorus (TRP) concentration in run-off water from an Index 3 soil at three different flow rates.

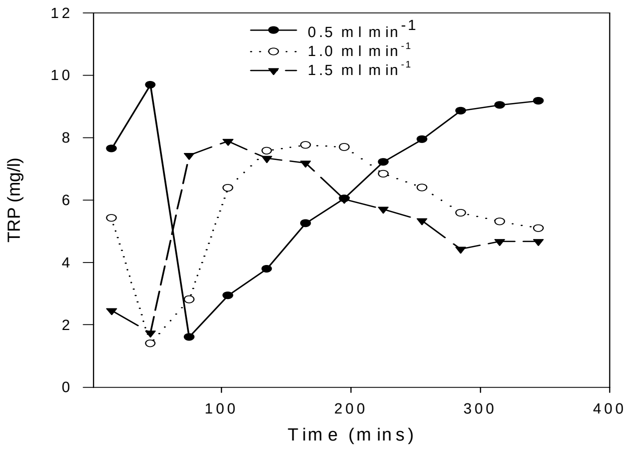

Figure 3.7. Temporal trends in total reactive phosphorus (TRP) concentration in run-off water from an Index 4 soil at three different flow rates.

Table 3.1. Coefficients of determination (R^2) between observed P concentrations and those estimated by Eqn 1 (see Section 3.2).

STP (mg/l)	Flow rate (ml/min)		
	0.5	**1.0**	**1.5**
2.8	0.968	0.889	0.950
6.2	0.971	0.938	0.976
9.6	0.992	0.956	0.929
29.8	0.992	0.665	0.805

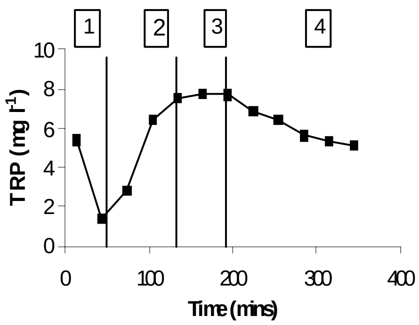

Figure 3.8. The four phases of total reactive phosphorus (TRP) export from the column during a continuous flow experiment.

between the STP and the inverse of the flow rate (R^2 = 0.98; $p < 0.001$), with coefficients of 0.0049 (per min) and 0.00171 (l/min^2), respectively. This indicates that the maximum rate of change in P concentration was positively related to STP and was magnified at higher flow rates (Fig. 3.9). Therefore, as flow and STP are increased the rate of change in TRP concentration from the column increases during Phase 2 of the experiment.

Multiple linear regressions showed that the maximum TRP concentration, which generally occurred during Phase 3, was strongly and significantly related to the STP, and the interaction of the STP and the inverse of the flow rate (R^2 = 0.96; $p < 0.001$), with coefficients of 0.152 (no dimensions) and 0.140 (l/min), respectively. This indicates that the maximum TRP concentration increased with higher STP values, and that this increase was strongest at the lower flow rate, and reduced at higher flow rates due to dilution (Fig. 3.10). The relationship between STP and P (TP, TDP, TRP, DRP, PP, DOP) concentrations has been documented by a number of authors, who have demonstrated a strong correlation between P concentration in overland flow and STP concentration (Sharpley, 1995; Pote *et al*., 1999a).

The significant impact of an increase in flow rate on the rate of change in TRP concentration during Phase 2 (Fig. 3.8) of the experiment may be due to the initial wash out of the resident soil solution P (TP, TDP, TRP, DRP) by the incoming solution. This increased the P concentration gradient between the soil particles and the soil solution and so P desorbed into the soil solution to re-establish equilibrium, and continued to do so until a maximum rate of P desorption (MRPD) is reached. The higher the flow rate, desorbed P is removed more rapidly and so will not impact on further desorption. At a lower flow rate, P is not removed as rapidly and so decreases the concentration gradient. As in infinite sink methods, such as the iron (Fe) oxide strip method (Frossard *et al*., 2000), the continuous flow of solution through the soil decreases the impact that desorbed P has on the further desorption of P from the soil. If the flow rate is sufficiently high and is providing an infinite sink for P desorption, then P desorption would be limited by film/intra-particle diffusion, hence the MRPD results in a plateau in the P concentration and so any further increase in flow rate may not result in an increase in desorption.

The results from the continuous flow experiment show that flow rate has an impact on P desorption at this scale. However, when this hypothesis was then tested at laboratory flume scale the impact of flow rate on P desorption was no longer evident. An increase in flow rate at laboratory flume scale resulted in a decrease in P (TDP, TRP, DRP) concentration due to dilution (Fig. 3.11). This was because of an increase in the system's complexity and a change in the dominant factors controlling P loss in overland flow. Physico–chemical processes may no longer be the dominant influence as transport factors such as overland flow volume and flow path length have an impact on the concentration of P (TP, TDP, TRP, DRP, PP, DOP) recorded in overland flow.

Results from a 26-h continuous flow experiment indicated that the TRP concentration declined gradually at all four STP concentrations after 26 h (Fig. 3.12). This suggests the possible existence of two distinct P pools. The initial P desorbed is sorbed at low-energy binding sites and so is freely available for desorption. Once this pool of freely available P is exhausted, dissolution of P controls the rate of P loss. Dissolution is a slower process and so P concentration then decreases gradually. This is supported

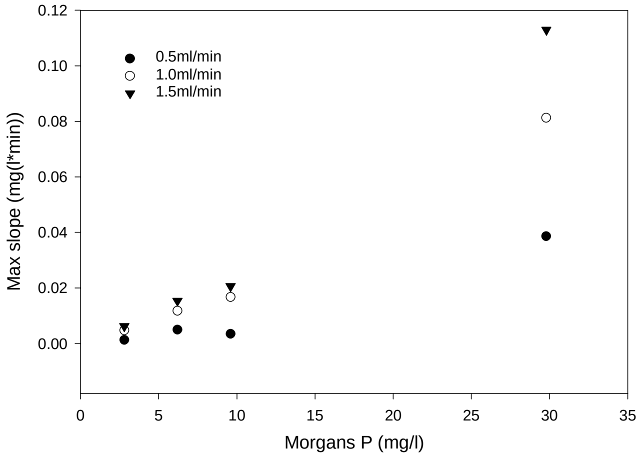

Figure 3.9. The impact of STP (Morgan's P) and flow rate on total reactive phosphorus (TRP) concentration.

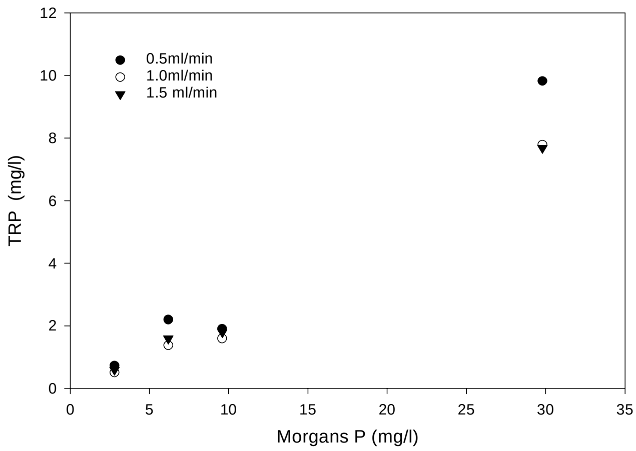

Figure 3.10. The impact of STP (Morgan's P) and flow rate on the maximum total reactive phosphorus (TRP) concentration.

by findings from previous work in which the existence of these two distinct pools was suggested (Maguire *et al*., 2001; Vadas and Sims, 2002).

The pool of freely available P is probably the major contributor to potential mobile P (PMP) in soil (Haygarth and Jarvis, 1999). If the source of freely available P is depleted the potential mobility of P decreases. This is important when put in the context of the increase in P concentration with increasing flow path length demonstrated at laboratory scale (Fig. 3.13). It is likely that one of the main reasons for this increase in P (TDP, TRP, DRP) concentration with an increase in flow path length was that as the area of saturation increased new areas of freely desorbable P are constantly accessed and so there was no depletion of the source of PMP. As the area of saturation increases and new areas of freely desorbable P are accessed, the pool of freely desorbable P rapidly desorbs from the soil due to the large concentration gradient. This rapid desorption of P due to a high concentration gradient is similar to what occurred during Phase 2 of the continuous flow experiment (Fig. 3.8). There was an increase in TRP concentration from the soil column during Phase 2 of the continuous flow experiment as the pool of freely desorbable P rapidly desorbs due to the large concentration gradient. This rapid desorption of freely desorbable P, combined with a minimal impact of dilution, resulted in the concentration of P increasing with flow path length during the laboratory flume experiment.

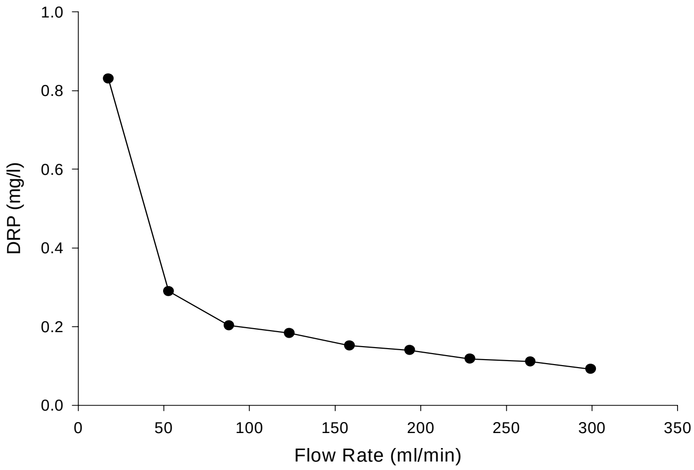

Figure 3.11. Variation in dissolved reactive P (DRP) concentration from an Index 4 soil with increasing overland flow rate and a steady flow path length at laboratory flume scale.

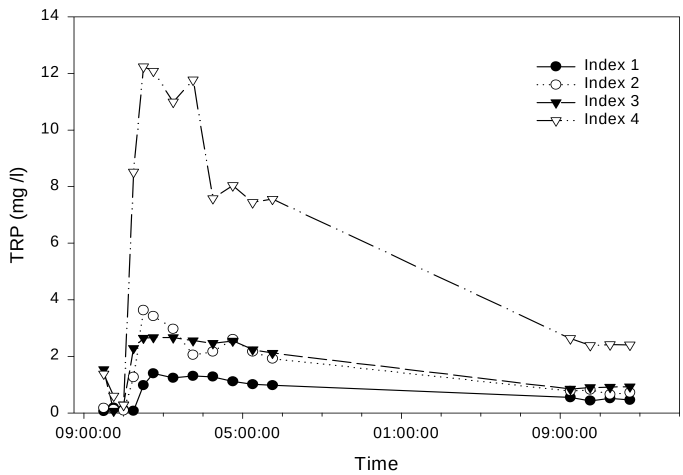

Figure 3.12. Temporal trends over a 26-h period in total reactive P (TRP) concentration from P Index 1, 2, 3 and 4 soils at a flow rate of 1 ml/min.

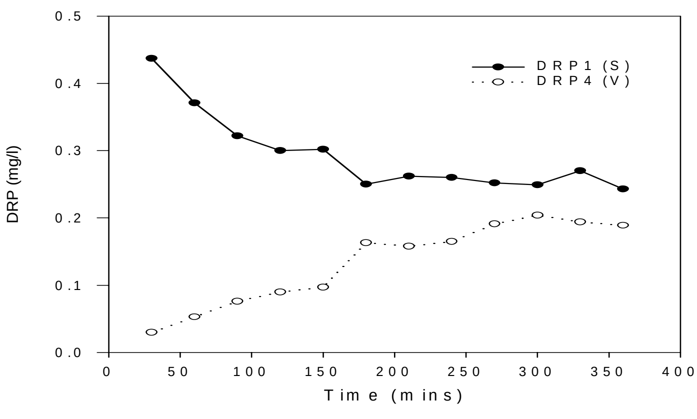

Figure 3.13. The impact of increasing flow path length (V) and steady flow path length (S) on DRP concentration from two simulated overland flow events at 88 ml/min flow rate from an Index 4 soil.

3.3 Soil Processes

3.3.1 Soil test P

Soil test P was one of the main source factors investigated in this study. Previous studies had found P (TP, TDP, TRP, DRP, PP, DOP) concentrations in overland flow increase with an increase in STP (Sharpley, 1995; Pote et al., 1999a; Tunney *et al.*, 2000; McDowell *et al.*, 2001). In the present study, STP also had a significant impact on the TRP concentration (Fig. 3.3). A similar relationship was observed in the laboratory flume experiment (Fig. 3.14). As the soil becomes increasingly saturated with P, at increasing STP, a higher percentage of P remains in soluble P form or is held in low-energy bonds as labile P (Kuo and Lotse, 1974), hence providing a higher percentage of PMP in the soil. Soil test P affects the concentration of P (TP, TDP, TRP, DRP, PP, DOP) exported during the continuous flow and laboratory flume experiments. However, the relationship between flow rate and P desorption during the continuous flow experiment and between flow path length and P (TDP, TRP, DRP) loss during the laboratory flume experiment occurs irrespective of STP levels.

3.3.2 Drying/re-wetting

Another important soil process that was investigated during this study was the impact of soil drying/re-wetting. During the continuous flow experiment when TDP concentration from field moist soil was compared against that of dried/re-wetted soil, the dried/re-wetted soil had a higher concentration of TDP exported from the column throughout the experiment (Fig. 3.15). In all the continuous flow experiments there was an initial high concentration of P (TP, TDP, TRP, DRP, PP, DOP) that decreased during Phase 1 of the experiment (Fig. 3.8). In a continuous flow experiment where the different P fractions were examined, dissolved organic P (DOP) contributed most of TDP during Phase 1 (Fig. 3.16). The contribution of DOP to TDP gradually decreased during this time, until Phase 2 of the experiment when DRP became the dominant fraction exported. The results from this drying/re-wetting experiment are in agreement with those of Turner and Haygarth (2001), who found that there is an increase in the availability of P after drying/re-wetting due to the lysing of microbial cells. Drying/re-wetting of soil releases large quantities of low available organic P from microbial cells into soil solution where it is freely available to become PMP.

When the impact of drying/re-wetting was examined at the laboratory flume scale, the concentrations of TDP, DRP and DOP increased with drying time. As the drying time was increased from 1 to 8 days there was a significant increase in the concentrations of TDP, DRP and DOP in overland flow (Table 3.3) ($p < 0.05$). However, at the field flume scale, overall, no relationship was found between soil moisture or time between overland flow events on TDP, DRP or DOP concentrations in overland flow.

Although no relationship was found between P (TP, TDP, TRP, DRP, PP, DOP) concentration and drying/re-wetting cycles in the soil at field flume scale, drying/re-wetting cycles in the soil may still play a role in the increase in P concentration with flow. Kurz (2002) found that the initial dissolved P concentration peak during an overland flow event was higher than subsequent peaks. This may be due to the initial release of PMP from microbial cells during the re-wetting of the soil. At field scale, Pote *et al.* (1999b) examined the impact of season on dissolved P concentration in overland flow and found that the concentration of dissolved P was higher during August than during May and concluded that this was due to warmer drier weather during the month of August. Sharpley (1980) investigated the impact of time interval between rainfall events on dissolved P concentration in overland flow and found that the concentration of dissolved P increased with time interval and this was attributed to phosphatase activity and the mineralisation of organic P. Although the hypothesis that drying/re-wetting cycles play a role in the increase in dissolved P concentration with flow was rejected at field flume scale, evidence from the literature would suggest that this requires further investigation. The data from this study suggest that it does not impact on the concentration of dissolved P recorded during individual events although it may still have an impact over a longer time frame.

3.4 Transport Processes

The transport processes provide the energy and the carrier for PMP to be exported from the soil to lakes and rivers. Only overland flow was investigated during this study as it is considered to be the main pathway of dissolved P loss from soil to water (Sharpley *et al.*, 1994). Rainfall duration, intensity and time interval between events were also identified as key factors in the transport of P from soil to water.

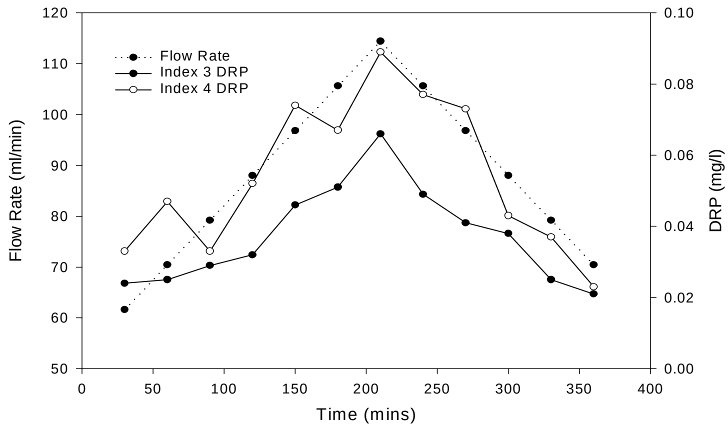

Figure 3.14. Temporal trends in DRP concentration in run-off water from soils with a P Index of 3 and 4 in response to changes in flow rate and flow path length.

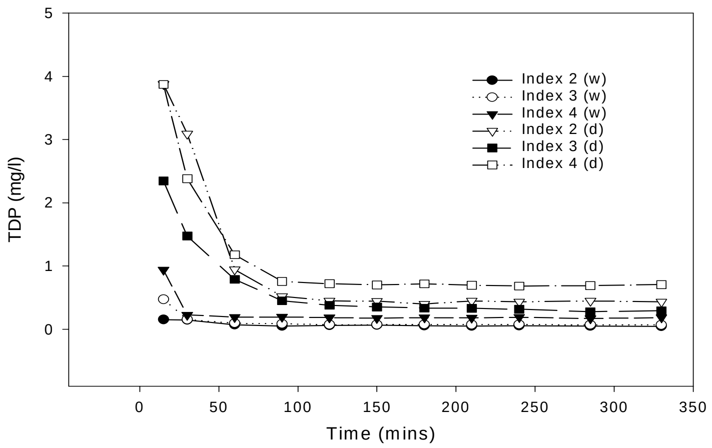

Figure 3.15. Temporal trends in total dissolved P (TDP) concentration in run-off from wet soil (w) and dry/re-wetted soil (d) at three soil P Index levels at a 1 ml/min flow rate.

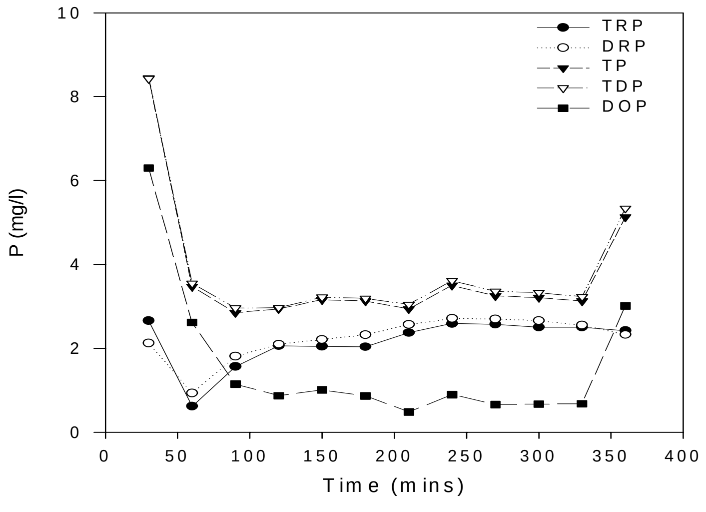

Figure 3.16. Temporal trends in concentration of total P (TP), total dissolved P (TDP), dissolved reactive P (DRP), total reactive P (TRP) and dissolved organic P (DOP) from an Index 3 soil at a flow rate of 1 ml/min.

Table 3.2. The impact of flow path length and flow rate on the P fractions recorded in the simulated overland flow experiment from multiple linear regression analysis.

P fraction	Independent variable	Intercept	Slope	R^2	p Value
DRP	Flow path Flow rate	0.056452***	0.000724*** –0.00049***	0.837214	<0.01
TDP	Flow path Flow rate	0.089913***	0.000702*** –0.0054***	0.789664	<0.01
DOP	Flow path Flow rate	0.033772	–0.000025 –0.000044	0.014006	n.s.

***Highly significant; n.s, not significant.

Table 3.3. The impact of flow path length and drying time on the P fractions recorded in the simulated overland flow experiment from multiple linear regression analysis.

P fraction	Independent variable	Intercept	Slope	R^2	p Value
DRP	Flow path Drying time	–0.00528	0.000665*** 0.008736***	0.855094	<0.01
TDP	Flow path Drying time	0.01484	0.000645*** 0.012967***	0.85376	<0.01
TP	Flow path Drying time	0.102855**	0.001102 –0.02129	0.328848	n.s.
PP	Flow path Drying time	0.093643***	0.000396 –0.03197**	0.093643	n.s.
DOP	Flow path Drying time	0.021463**	0.000022 0.004108***	0.20394	n.s.

***Highly significant; n.s, not significant.

Time between events has an impact on the formation of the hydrological pathways, through its determination of antecedent soil moisture conditions. The soil moisture data from the field flume experiment confirmed that saturation excess is the main form of overland flow occurring at the site monitored. Except for one recorded event, overland flow was not initiated within the field flume until a soil saturation level of approximately 50% was reached (Table 3.4). The soil saturation value at which overland flow occurred during each event was at or close to the maximum level of soil saturation achieved during an event. During one event, infiltration excess overland flow may have occurred. Infiltration excess overland flow often occurs due to high rainfall intensities that exceed the infiltration rate of the soil. At lower rainfall intensities, infiltration excess overland flow can take place due to processes such as surface sealing, which can occur under dry soil conditions. During the one rainfall event during which infiltration excess occurred, the soil moisture was very low and did not change until after the overland flow had taken place (Fig. 3.17). Surprisingly, this happened at low rainfall intensity and therefore is assumed to be due to surface sealing and not due to the rainfall rate exceeding the infiltration rate of the soil (Ward and Robinson, 1990).

VSA theory indicates that the areas of saturation from which overland flow originates rapidly expand and contract during rainfall events (Dunne and Black, 1970; Pionke et al., 1988; Gburek and Sharpley, 1998). This was clearly occurring at both field flume and field scale, where there is a rapid expansion of the area of saturation during rainfall events. Figure 3.18 demonstrates a comparison of the overland flow data from the edge-of-field monitoring point and from the field flume for an event on 2 May. Overland flow was recorded at both the edge-of-field monitoring point and the 10 m × 1 m field flume located roughly 20–25 m upslope from the edge-of-field monitoring point. Overland flow at the edge-of-field monitoring point starts 4 h before overland flow is recorded from the field flume and continues from the field site roughly 7 h after overland flow finishes from the field flume. This trend is consistent throughout all recorded events where flow occurred from the field site and the field flume although the timing of the events varies. This would support the theory that VSAs are expanding upslope

Table 3.4. The P fractions and flow data for 18 overland flow events monitored from the 10 m × 1 m field plot.

Date	TP (mg/l)	TRP (mg/l)	PP (mg/l)	TDP (mg/l)	DRP (mg/l)	DOP (mg/l)	Total flow (l)	% of total TP exported	% of total TRP exported	% of total overland flow exported
20/01/2003	–	11.6	–	–	8.8	–	182.5	–	1.6	3.6
07/03/2003	–	8.6	–	–	7.6	–	201.9	–	1.2	4.0
14/04/2003	151.8	30.6	74.2	77.6	29.3	48.3	218.2	9.5	4.1	4.4
25/04/2003	45.3	10.8	20.8	24.6	10.4	14.2	67.6	2.8	1.5	1.3
02/05/2003	93.8	35.7	47.4	46.4	34.9	11.5	234.8	5.9	4.8	4.7
03/05/2003	54.8	17.5	30.1	24.7	16.8	8.0	135.6	3.4	2.4	2.7
04/05/2003	10.0	1.9	5.6	4.3	1.8	2.5	32.7	0.6	0.3	0.7
03/06/2003	63.0	19.1	27.4	35.5	19.7	15.9	193.8	3.9	2.6	3.9
10/06/2003	341.4	178.1	108.1	233.4	165.7	68.8	1060.1	21.3	24.1	21.1
24/07/2003	28.1	14.6	6.1	22.0	11.9	10.1	122.5	1.8	2.0	2.4
30/10/2003	66.2	51.1	–	–	–	–	199.7	4.1	6.9	4.0
31/10/2003	271.4	180.7	–	–	–	–	1066.9	16.9	24.4	21.3
13/11/2003	105.3	32.7	39.6	65.7	32.5	33.2	297.0	6.6	4.4	5.9
01/12/2003	34.2	16.7	14.8	19.5	17.3	2.2	101.2	2.1	2.3	2.0
02/12/2003	28.1	13.8	13.6	14.5	13.5	1.0	94.1	1.8	1.9	1.9
11/12/2003	164.7	70.1	72.4	92.4	70.1	22.3	439.4	10.3	9.5	8.8
12/12/2003	108.1	28.0	62.1	45.9	31.3	14.6	265.0	6.7	3.8	5.3
22/12/2003	35.4	17.5	–	–	–	–	99.5	2.2	2.4	2.0

–, Not recorded.

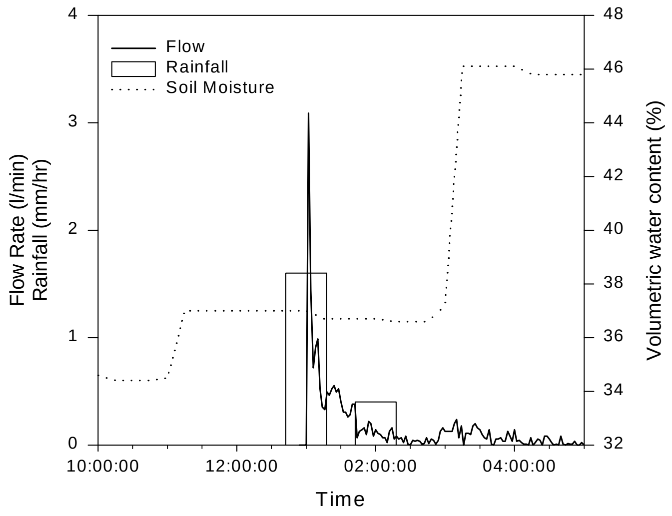

Figure 3.17. Change in soil moisture and overland flow from the 10 m × 1 m field plot during rainfall on 1 July 2003.

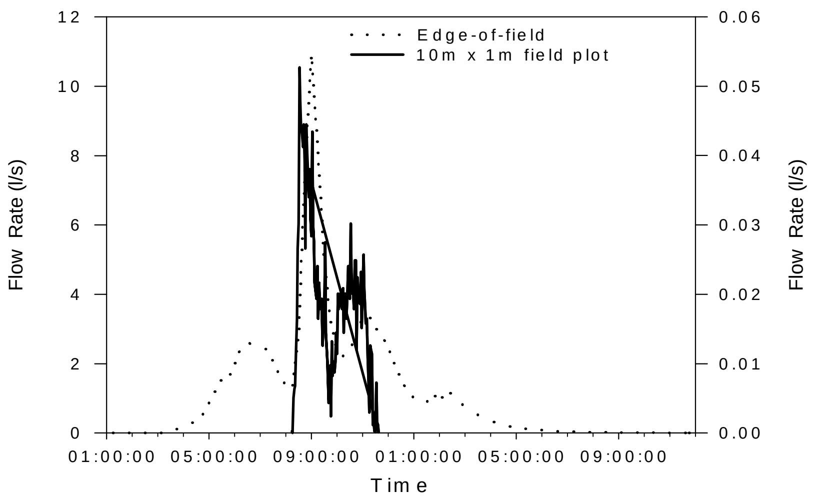

Figure 3.18. Comparison of the timing of overland flow from the edge-of-field (primary y-axis) and overland flow from the 10 m × 1 m field flume (second y-axis) on 2 May 2003.

during a rainfall event and that when it expands as far as the field flume, overland flow is recorded from the field flume. There were a number of events where flow was measured from the field site but not at the field flume plot, suggesting that during some events the VSAs did not expand upslope as far as the field flume.

Changes in soil moisture upslope in the 10 m × 1 m plot during a number of events are shown in Figs 3.19 to 3.22. As can be seen, as the events progress there is an advance of the wetting front upslope. This is again consistent with VSA theory. During many of the events the wetting front did not advance far, as for example during the event recorded on 2 December 2002 (Fig. 3.20). However, on 30–31 December 2002 and 9–10 June 2003 events, which collectively contributed nearly 50% of the total TRP export and 43% of the total overland flow from the site, the wetting fronts advanced far up the slope to a distance of approximately 3 m above the position of probe 1 (Figs 3.20 and 3.22). Tables 3.5 and 3.6 show the P concentration, rainfall and soil moisture data for all the events monitored from the field flume.

As this area is expanding, it is also increasing the source area that has access to the energy/carrier required to transport PMP from the soil. This expansion in the zone of

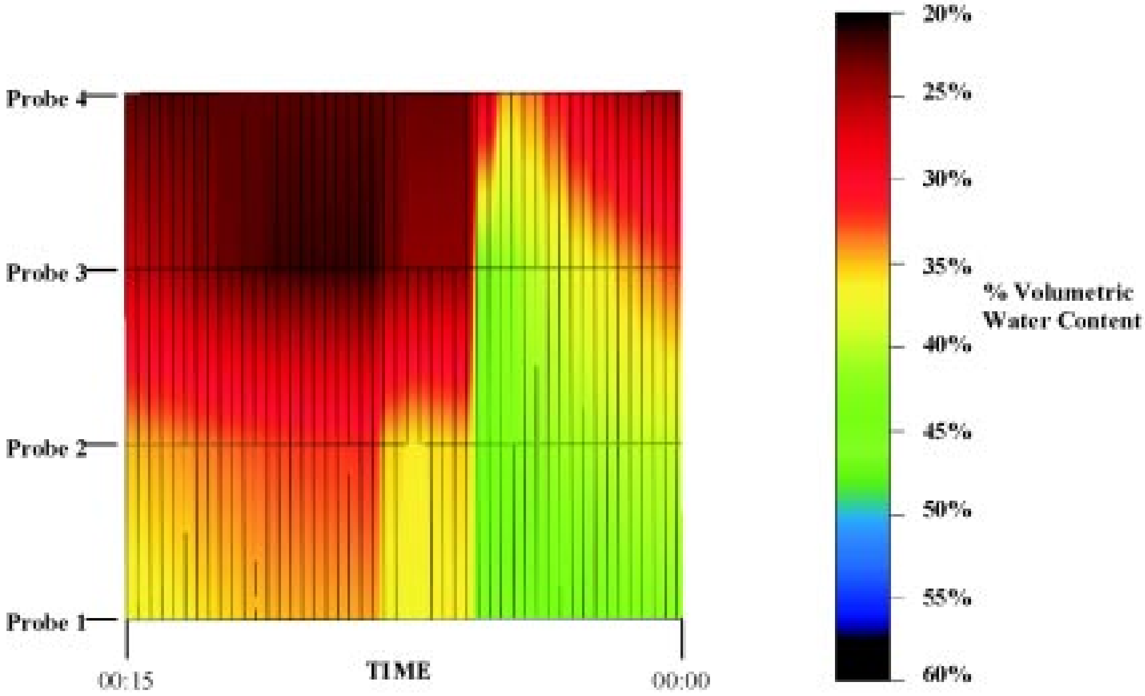

Figure 3.19. Change in percentage volumetric soil water content for four TDR probes at 2-m intervals in the 10 m × 1 m field plot during rainfall on 1 July 2003.

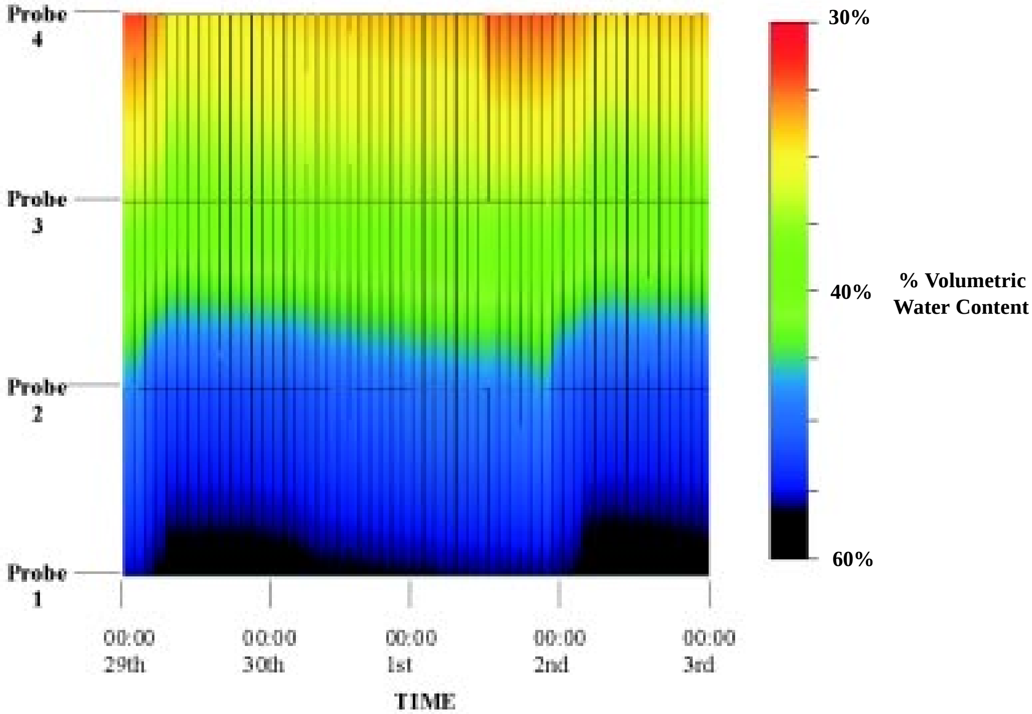

Figure 3.20. Change in percentage volumetric soil water content for four TDR probes at 2-m intervals in the 10 m × 1 m field plot during two rainfall events from 29 November to 2 December 2003.

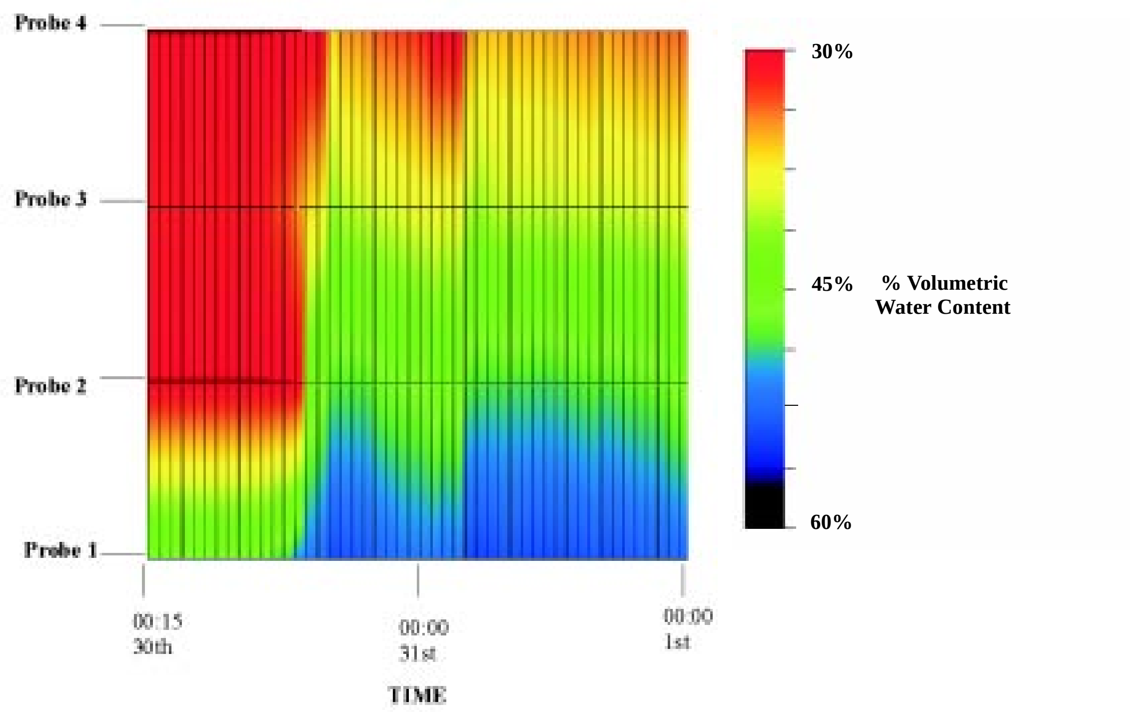

Figure 3.21. Change in percentage volumetric soil water content for four TDR probes at 2-m intervals in the 10 m × 1 m field plot during two rainfall events in October 2003

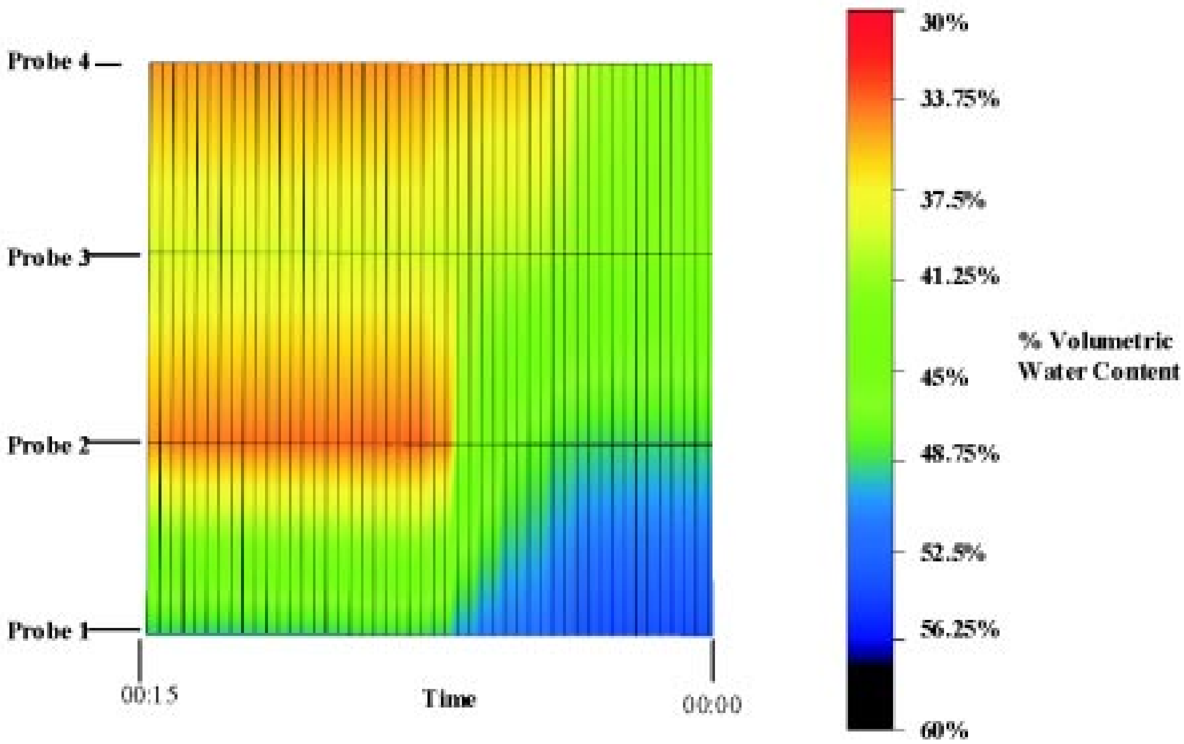

Figure 3.22. Change in percentage volumetric soil water content for four TDR probes at 2-m intervals in the 10 m × 1 m field plot during a rainfall event on 9 June 2003.

Table 3.5. Meteorological and soil moisture data from 18 overland flow events monitored from the 10 m × 1 m field plot.

Date	Soil moisture deficit*	Evaporation (mm)	Total rainfall (mm)	Event rainfall (mm)	Initial soil moisture (%)	Soil moisture at the start of overland flow (%)	Max. soil moisture (%)	Days between overland flow events
20/01/2003	–10.0	0.8	16.4	10.4	–	–	–	1
07/03/2003	–10.0	0.9	9.4	6.0	–	–	–	3
14/04/2003	–10.0	1.0	13.2	6.4	36.3	45.4	52.9	2
25/04/2003	–8.5	1.0	12.4	7.8	49.1	52.2	53.2	4
02/05/2003	–9.3	1.2	24.4	9.8	–	–	–	4
03/05/2003	–7.8	1.1	29.8	20.0	–	–	–	1
04/05/2003	–10.0	0.8	8.2	4.2	–	–	–	1
03/06/2003	–5.2	0.8	11.4	7.8	48.3	49.9	51.7	11
10/06/2003	2.0	1.0	22.8	19.4	49.1	51.1	53.8	3
24/07/2003	–3.9	1.2	11.8	8.6	–	–	–	4
30/10/2003	–8.5	1.0	27.4	10.2	46.4	52.0	53.9	42
31/10/2003	–7.3	0.7	23.8	21.4	51.3	51.5	54.1	1
13/11/2003	–10.0	1.1	17.6	10.0	56.5	58.2	58.3	12
01/12/2003	–4.4	0.9	15.2	12.8	56.7	57.6	58.4	1
02/12/2003	–3.2	0.9	12.4	9.6	57.3	58.5	58.6	1
11/12/2003	–8.4	1.1	17.2	16.0	56.9	57.3	58.2	1
12/12/2003	–6.8	1.2	9.0	7.0	58.0	58.0	58.1	1
22/12/2003	–3.1	0.7	16.4	12.6	55.9	57.7	58.1	1

*A soil moisture deficit of –10 indicates the soil is fully saturated; –, not recorded.
All soil moisture data presented are from TDR probe 1, located furthest downslope in the 10 m × 1 m field plot.

Table 3.6. Particulate P (PP), flow and rainfall data during 13 overland flow events monitored from the 10 m × 1m field plot.

Date	Average % PP contribution to TP	Max. % PP contribution to TP	Total flow (l)	Max. flow rate (l/min)	Total rainfall (mm)	Max. 5 min intensity (mm/h)	Max. 15 min intensity (mm/h)
14/04/03	48.9	60.9	218.2	2.3	13.2	2	–
25/04/03	45.8	64.2	67.6	1.5	12.4	4	–
02/05/03	50.5	58.6	234.8	3.2	24.4	6	–
03/05/03	54.9	71.6	135.6	1.5	29.8	6	–
04/05/03	56.5	65.9	32.7	1.1	8.2	4	–
03/06/03	43.6	58.5	193.8	3.5	11.4	8	–
10/06/03	31.7	69.3	1060.1	3.3	22.8	4	–
24/07/03	21.6	49.5	122.5	2.3	11.8	6	–
13/10/03	37.6	49.4	297.0	2.5	17.6	8	7.2
01/12/03	43.1	52.6	101.2	0.6	15.2	6	4.8
02/12/03	48.4	56.4	94.1	1.4	12.4	8	7.2
11/12/03	43.9	62.9	439.4	2.5	17.2	6	4.8
12/12/03	57.5	82.7	265.0	4.3	9.0	8	9.6

–, Not recorded.

saturation also results in a change in the flow path length. The laboratory flume experiment was conducted to examine the impact of this increase in overland flow path length on P losses. The results from the laboratory flume experiments demonstrated that flow path length had a significant impact on P (TDP, TRP, DRP) concentration in overland flow (Table 3.2). As the flow path is increased there is an increase in DRP concentration recorded (Fig. 3.13). Where the flow path length is held constant throughout the duration of the experiment, DRP concentration decreases. The differences in the trends of the DRP concentrations between an increase and steady flow path may be due to the availability of freely desorbable P as discussed previously.

An increase in flow rate during the laboratory flume experiments resulted in a decrease in DRP concentration due to dilution (Fig. 3.23 and Table 3.2). This is similar to the inverse relationship between flow rate and dissolved P concentration discussed in Section 3.2. However, when flow rate was increased in conjunction with flow path length, the DRP concentration in overland flow still increased despite the increase in dilution. Conversely, the P (TDP, TRP, DRP) concentration in overland flow also decreased with a corresponding decrease in flow path length and therefore it was possible to replicate the relationship between P concentration and flow rate using this method at laboratory flume scale (Fig. 3.24). This would suggest that flow path length had a more dominant influence over P (TDP, TRP, DRP) concentration in overland flow than flow rate.

Although the laboratory flume experiment showed a significant relationship between flow path length and dissolved P concentration in overland flow no clear relationship was found between dissolved concentration in overland flow and the expansion of the saturated zone at field flume scale. However, as mentioned previously, two events (on 30–31 December and 9–10 June) of the 18 monitored from the field flume collectively contributed nearly 50% of the total TRP exported and 43% of the total overland flow from the site. These events also demonstrated the greatest advance of the wetting fronts upslope to a distance of approximately 3 m above the position of probe 1 (Figs 3.21 and 3.22). The hypothesis that an increase in flow path length resulted in an increase in dissolved concentration was accepted at laboratory flume scale. However, this could not be accepted or rejected at field flume scale due to inconclusive results under the conditions of this experiment.

3.5 Soil/Water Interface Processes

The two mobilisation processes occurring at the soil/water interface are mixing and erosion/entrainment. Results from the laboratory and field flumes provided important information on the mobilisation processes occurring at the soil/water interface. Mixing was identified as the key mobilisation process in agricultural grassland. However, results from the laboratory and field flume experiments suggest that soil erosion/entrainment may also play an important role in the mobilisation of PMP.

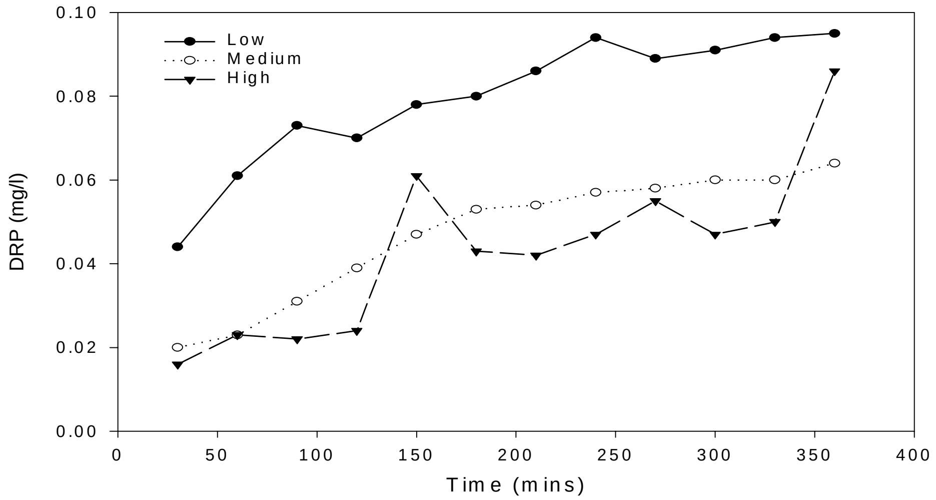

Figure 3.23. Variation in DRP concentration from an Index 3 soil during three simulated overland flow events with increasing flow path length at three different flow volumes (low, medium and high).

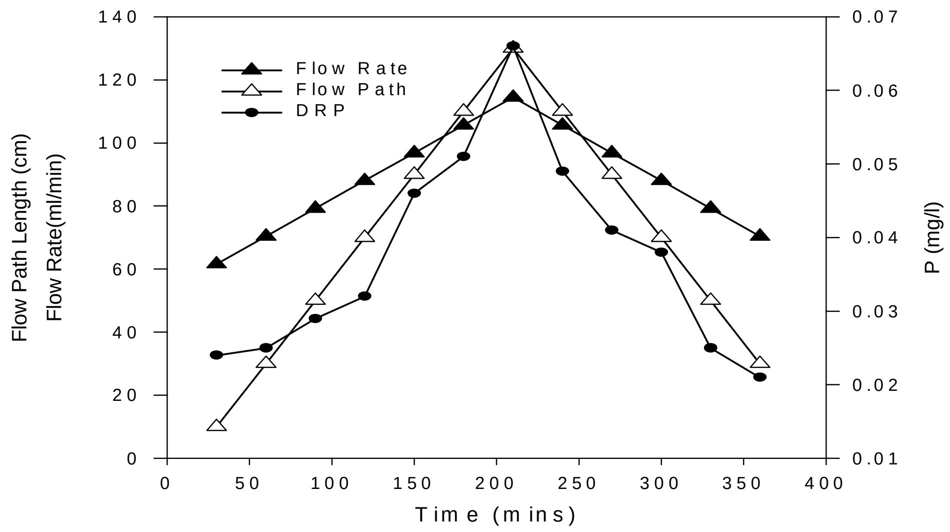

Figure 3.24. Variation in DRP concentration with an increasing and decreasing flow path length during simulated overland flow experiments on Index 3 soils

The average PP contributions to TP for the laboratory and field flume experiments were 52.1% and 44.9%, respectively. In both cases, the influence of the experimental methods on erosion processes cannot be dismissed. However, during both experiments, significant quantities of PP were transported in overland flow. The influence of the disturbance would be expected to decrease with time as the grass sward re-establishes itself and the soil stabilises. During the lab flume experiment, the PP contribution to TP generally decreased with increasing flow path length, due to an increase in the filtering efficiency of the grass sward with flow path length. This is in agreement with the work of Deletic (1999) and Fogle *et al.* (1994) who concluded that the filtering capacity of the grass sward increases with increasing flow length.

An unusually high contribution of PP to TP was also evident during overland flow events monitored in the field flume (Table 3.6). Generally, the contribution of PP to edge-of-field losses from grasslands is not greater than 30% (Kurz, 2002). It was not possible to make a direct comparison between the PP losses at field flume scale and PP losses at the edge-of-field monitoring point. However, a previous study (Kurz, 2002) gave an average PP contribution to TP of 23% for the monitored sites within Johnstown Castle where the study presented here was also carried out.

Grass filter strip studies have demonstrated that significant quantities of PP can be transported over distances of less than 10–15 m (Fogle *et al.*, 1994; Deletic, 1999). In the laboratory flume experiment, the longest possible flow path length was 2.2 m. In the field flume experiment, the maximum flow path length was 10 m. In contrast, at field scale, there is a greater area of saturation and hence a greater volume of rainfall contributing to overland flow, while the area that will contribute significant quantities of PP is still limited to 10–15 m from the edge-of-field monitoring point. The resulting PP transported within this 10- to 15-m distance is diluted by the water draining from the greater area contributing to overland flow.

Although the data are not available from this work, it is possible to hypothesise that P desorbed from the large quantities of PP entrained in overland flow within the grass may be making a significant contribution to dissolved P measured in edge-of-field losses. Where soil particles are entrained in overland flow, due to mixing and the large soil/water ratio causing a large concentration gradient, P would desorb from the soil particles into overland flow. Work carried out by Sharpley *et al.* (1981) demonstrated that the reverse can occur where soil particles entrained in overland flow can re-adsorb dissolved P in overland flow. Further work is needed to test the hypothesis that soil particles entrained in overland flow are a source of PMP and make a significant contribution to dissolved P edge-of-field losses from agricultural grasslands.

3.6 Summary

The approach taken during this project was to use small-scale studies to develop hypotheses that can then be tested at field scale. Caution needs to be used when using results from small-scale studies to explain field/catchment scale processes. However, a better understanding was obtained of the processes involved in an increase in P concentration with an increase in overland flow.

All of the processes discussed play a key role in the loss of P from soil to water. If the hypotheses developed during the laboratory experiment hold true at field scale then VSA hydrology controls the increase in P concentration with an increase in overland flow rate. It is important to note that, although VSA hydrology is possibly the controlling factor in the relationship, it is the interaction between the transport, soil, physico–chemical and soil/water interface processes that results in environmentally significant quantities of P being exported. The expansion of the VSA means that the pool of freely desorbable P is not depleted. Variations in the STP and drying/re-wetting cycles of the soil (source component) change the fraction and quantities of P exported. It is only when these three components interact at the soil/water interface that there is an increase in P concentration with an increase in overland flow rate.

4 Conclusions

4.1 Continuous Flow Experiments

- Flow rate had a statistically significant impact on TRP concentration. However, it was only during Phase 2 of the experiment when TRP concentration is increasing up to a maximum rate of P desorption. Once a maximum rate of P desorption has been reached any further increase in flow rate results in dilution.
- There was a significant correlation between STP and TRP concentrations in the effluent from the soil column.
- Drying/re-wetting of soil samples resulted in an increase in dissolved TDP concentration recorded.
- Two pools of P are available for desorption. The first is freely available P that can be rapidly desorbed from the soil and is depleted in a number of hours. In the second pool, the rate of desorption is limited by dissolution of P, and therefore is a slower process that occurs over a longer period of time.

4.2 Laboratory Flume Experiment

- An increase in flow path length resulted in an increase in TDP, DRP and TRP concentrations in overland flow.
- An increase in flow rate resulted in the dilution of TDP, DRP and TRP concentrations in overland flow.
- When an increase in flow rate was accompanied by an increase in flow path length, TDP, DRP and TRP concentrations increase, despite the effects of dilution.
- An increase in soil drying time resulted in an increase in P (TDP, TRP, DRP) concentration in overland flow.

4.3 Field Flume Experiment

- An increase in P (TDP, TRP, DRP) concentration with flow occurs during some of the overland flow events monitored in the flume. However, it is not clear why it did not occur during all the overland flow events.
- During the 18 overland flow events monitored, no relationships were found between soil moisture or time between events and P (TP, TDP, TRP, DRP, PP, DOP) loss in overland flow from the 10 m × 1 m plot.
- Four rainfall events accounted for 58% of TP, 62.2% of TRP exported, and 55.5% of the corresponding total flow recorded from the plot.
- Saturation excess overland flow was the dominant overland flow type in the flume. However, infiltration excess overland did occur during one event.
- During rainfall events the zone of saturation in the field site and in the field flume expanded upslope increasing the area within the field and the plot that were contributing to overland flow. However, no relationship was found between the expansion of the area of saturation and P (TP, TDP, TRP, DRP, PP, DOP) concentration in overland flow.
- Particulate P contributed a higher percentage of TP from the 10 m × 1 m field plot than is generally reported at edge-of-field losses.
- Overland flow path length within the 10-m long flume was a maximum of 5–6 m
- Significant quantities of PP can be mobilised and transported in overland flow in grassland over short distances.

4.4 Overall Conclusions

- Hypotheses accepted during small-scale experiments need to be tested at field/catchment scale.
- The existence of a freely desorbable pool of P plays a vital role in the availability of PMP for P loss in overland flow.
- As a VSA expands, it also increases the source area that has access to the energy/carrier required to transport PMP from the soil. This results in a corresponding increase in the critical source areas of P loss.
- Drying/re-wetting cycles in soil increase the quantity and change the forms of P available as PMP in soil.
- There is a significant correlation between STP and P loss in overland flow.

- Significant quantities of PP can be mobilised, entrained and transported over short distances in overland flow. The contribution of P desorbed from soil particles entrained in overland flow to dissolved P edge-of-field losses is not known.

- The findings from this work suggested that the interaction of VSA hydrology with the pool of freely desorbable P in the soil is responsible for the increase in P concentration with an increase in overland flow.

- Further work is required to verify these results at field and catchment scales.

4.5 Recommendations

The results of this research indicate that during rainfall the expanding overland flow areas (VSAs) combine with soils that have high levels of potentially mobile P (PMP) to form critical source areas of P loss from soil. It is recommended that catchment-scale physical modelling of P concentrations in water take the processes outlined here into account in order to improve the accuracy of model predictions and to assist in identifying potential critical source areas within catchments. It is also recommended that these critical source areas be identified at field scale so that measures to limit P loss from soil to water can focus on these areas.

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