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EUTROPHICATION FROM AGRICULTURAL SOURCES

Environmental Soil Phosphorus Test

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Final Report

Prepared for the Environmental Protection Agency

by

Teagasc, Johnstown Castle, Wexford

Authors:

Karen Daly and Anne Casey

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

Karen Daly
Teagasc
Johnstown Castle Research Centre
Co. Wexford

Tel: +353-53-42888
E-mail: kdaly@johnstown.teagasc.ie

Anne Casey
Teagasc
Johnstown Castle Research Centre
Co. Wexford

Tel: +353-53-42888
E-mail: acasey@johnstown.teagasc.ie

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Executive Summary

Introduction

Phosphorus loss from soil to water is a major component of surface-water pollution in Ireland and water quality reports from the EPA have shown an increasing upward trend in slight and moderate pollution often attributed to agricultural phosphorus (P). There is a need, therefore, for indicators of P loss from agriculture that can be related to water quality, such as models and risk assessment tools that might predict areas vulnerable to P loss. Soil test P is a typical parameter often used in risk assessment and catchment modelling and although originally designed as an agronomic indicator of P requirements for crop growth, it is often used to indicate risk of P loss from agricultural areas.

Soil P testing in Ireland uses the Morgan's P test to extract plant-available P as an indicator of crop requirements for fertiliser advice. This test uses an acidic extract on soils sampled to 10 cm and has been used in the context of potential losses of P from soil to water. In Europe and the United States, there have been a number of alternative or environmental soil-test procedures developed as indicators of soil P loss that focus on simulating desorption and solubilisation of P from soil to solution. These procedures generally require a mild extractant, such as water or calcium chloride, in an attempt to simulate overland flow concentrations and often require shallow sampling depths and wider solution-to-soil ratios than agronomic P tests. In addition, the use of P saturation as an environmental indicator has also been used to assess potential P loss from soils since it is a measure of P concentration in soil relative to amounts of Al and Fe, which symbolise P saturation sites in soil.

This project attempted to place soil P testing in an environmental context by questioning conventional sample depth, sample pre-treatment, choice of extractant and extract ratios against a background of dissolved reactive P (DRP) and suspended solids (SS) concentrations monitored from the same sample sites. The work examined laboratory-scale soil P extraction techniques and field-scale P loss using soils sampled from sites at Johnstown Castle Wexford.

Methods

Soil samples were collected from seven grassland field sites at Johnstown Castle covering a range of soil P levels. These sites were chosen since they are subjected to continuous monitoring of overland flow during rainfall events and could provide already installed instrumentation for gathering information on edge-of-field P losses. Seven field sites provided soil samples for analysis and two of these sites were used to collect and analyse DRP and SS in overland flow.

Soil sampling included three sample depths, the agronomic depth to 10 cm and two shallow depths to 2 and 5 cm, as proposed by some environmental soil P tests. Soils were sampled in triplicate on each sampling occasion to assess spatial variation within and between sites against the variation in P concentrations at different sample depths.

Soil test P methods were chosen to represent some currently used agronomic and environmental extractants and these included Morgan's P (Pm), Mehlich-3 (PM3), iron-oxide paper strip P (Pfeo), water-soluble P (Pw) and calcium chloride P ($Pcacl_2$). Soils sampled at each depth were analysed using the above extractants, including analyses of Mehlich-3 extractable Al. Soil P saturation was calculated as the ratio of Mehlich-3 P to Mehlich-3 Al and expressed as a percentage (% Psat).

Water-to-soil ratios can varying during an overland flow event and can influence DRP concentrations collected during events. Soils sampled to each depth were subjected to varying water-to-soil ratios in the range of 5–250 l kg^{-1} to gauge the effect of widening water-to-soil ratios on laboratory extractable P. Recent work monitoring P loss from grassland fields found elevated DRP concentrations in events following periods of soil dryness. This work examined the effect of drying and re-wetting of soil on water-soluble P by extracting samples in field-moist and oven-dried (40°C) conditions over a range of water-to-soil ratios.

In this work, overland flow samples were collected from two of the seven sites used for soil sampling, during the winter months of December 2001 to March 2002. The two sites represented high and low P levels and samples collected continuously during this period were analysed for DRP, SS and flow rate.

Results and Discussion

The effect of sample depth on soil extractable P showed no clear and consistent trend in P concentration in soils sampled to 2, 5 and 10 cm. Statistical analysis of samples taken at each depth in triplicate showed that for each of the soil P tests used, statistically significant differences were not consistent. For example, Pw varied significantly with sample depth at only two sites whilst Morgan’s P varied with sample depth at five sites, mostly at the 5% level of probability. The indications from these data are that spatial variation within and between sites was too high to allow for consistent statistical differences in sample depth to be observed.

The relationship between % Psat and Pw was examined at each sample depth and higher R^2 values were observed in the relationship for soils sampled to 10 cm compared with 2 cm. Percentage P saturation is often quoted as an environmental indicator of water-soluble P loss and represents saturation and sorption aspects of soils. The higher R^2 value observed in its relationship with Pw, for samples taken to 10 cm, suggests that this sample depth provides a better representation of saturation and sorption potential than the surface soil to 2 cm. Furthermore, higher amounts of organic matter at the surface 2 cm compared with 10 cm were negatively correlated with amounts of extractable Al, indicating that P sorption may be inhibited at the surface and that samples taken to 10 cm present a more accurate reflection of the degree of P saturation within the soil matrix and hence potential losses to water

In the overland flow data at the high P site, SS correlated positively with DRP but only accounted for 18% of the variation in DRP values at this site. This relationship concurs with the findings of other workers who have suggested that a substantial part of DRP originates from the bulk of the soil remaining in the field and that eroded SS may only have a secondary importance. In terms of sample depth, the conventional 10-cm samples capture the bulk of the soil and potential P saturation and soluble P released to overland flow.

The effect of widening water-to-soil ratios on water extractable P on soils simulated a range of P concentrations and amounts of desorbable P. Phosphorus desorption from soil to water responded to water-to-soil ratios by increasing as water-to-soil ratios increased, illustrating chemical desorption from soil to solution. When samples were extracted under field-moist and oven-dried conditions, Pw increased by between 110 and 560% when samples were oven dried before extracting with water. Other workers have suggested that soluble P released upon re-wetting of dried soil is due to microbial cell rupture. The increase in Pw occurred over a range of water-to-soil ratios and correlated positively with increasing water-to-soil ratio, i.e. as water-to-soil ratios were widened the difference between wet and dry extraction increased. This suggests that microbial P release may not be the only explanation for the increase in water-soluble P and that some physico–chemical factors are also involved.

The range of DRP concentrations measured in overland flow could be simulated in the laboratory Pw extractions across the range of water-to-soil ratios for the high P site only and values of DRP from the low P site were too low to simulate in the laboratory. Therefore, to compare the sites and soil P tests in an environmental context, P loss and soil P were examined on a mass basis.

The field measurements of DRP in overland flow from the two sites were converted into annual P loadings (kg P ha^{-1}) and a 7-fold difference in P loss was observed between the sites. This concurs with other monitoring data in 1997–1998 from the same sites, which also found a 7-fold difference in export rates between the high and low P sites. To compare soil test P values from the range of tests used, P concentrations in soils were converted to kg P ha^{-1} and the relative difference in these values between sites calculated using soil P data for samples taken to 10 cm. In this instance, the difference in Morgan’s P (kg P ha^{-1}) was more comparable to the difference in annual export rates (kg P ha^{-1}) between the two sites than any other soil P tests examined.

The conclusions from this study suggest that the conventional sample depth to 10 cm is a better representation of the bulk soil and its saturation properties than shallow sample depths. In addition, a consistent statistical difference in P at various depths would need to be established to justify a change from the conventional agronomic depth.

Morgan’s P was compared against other agronomic and environmental soil P tests in relation to measured losses from field sites at Johnstown Castle and in this study provided the best indicator of P loss from the sites investigated.

1 Introduction

Diffuse losses of agricultural phosphorus (P) are a major component of surface-water pollution. Phosphorus in overland flow originating from grassland soils can exist in dissolved reactive and particulate form, with the former being more dominant. Losses to overland flow are typically measured by edge-of-field monitoring of the dissolved fraction. These are attributed to desorption of P from soil and losses of recently applied fertiliser and manure P, or incidental losses. Whilst incidental losses may be highlighted in monitoring data as exceptionally high concentrations in overland flow, the background or losses from soils are usually responsible for the remainder of the P loading. Relating soil P to losses in overland flow relies on a measure of soil P concentration as an indictor of potential loss usually employing soil P tests. These were originally designed as an indicator of plant-available P for crop growth and fertiliser recommendations. This has been a useful approach thus far and has proved successful in correlating edge-of-field losses to soil P level (Pote *et al*., 1999; Tunney *et al*., 2000). However, recently soil P testing in environmental studies has focussed on methods that simulate the process of P desorption in soils (Pote *et al*., 1996). This is the process whereby solid-phase P bound to sorption sites within the soil are solubilised or desorbed to solution, often into the soil solution for plant uptake but also to overland flow water during runoff events. Phosphorus desorption is usually measured with procedures that simulate P transfer into solution, such as water extractable P (Van der Paauw, 1971), calcium chloride extractable P (Houba *et al*., 1994) and more long-term desorption techniques, such as the iron-oxide impregnated paper strip test (Menon *et al*., 1988).

Relating soil P testing to losses in overland flow requires a closer look at some of the environmental aspects of soil P extractions and P concentrations in such flow. Dissolved reactive P (DRP) concentrations in overland flow can vary during and between runoff events (Kurz, 2002). This is possibly due to soil chemical and biological factors (drying and re-wetting, mineralisation of organic P and precipitation of inorganic P) and hydrological factors (rainfall intensity and soil hydraulic conductivity). Extractable soil P can also vary temporally and changes in soil biology, namely mineralisation and immobilisation of organic P, can lead to variations in soil P testing results, in conjunction with spatial variations on soil P at field level (Herlihy and O’Keeffe, 1983).

This work examined aspects of soil P testing that could be measured under laboratory conditions in the context of losses to water. It focussed on the chemistry of P loss from soils and how it related to observed DRP values from field measurements. Soil P desorption was assumed to account for losses to water other than incidental losses and factors affecting P desorption, such as soil sample depth, drying and re-wetting of soil and water-to-soil ratio, were examined. Turner and Haygarth (1999) suggested a protocol for potential P solubilisation during discussions on the development of an environmental soil P test within the COST 832 working group. The main features of the COST 832 protocol focused on shallow sample depths (2 cm and 5 cm), wide extract ratios and equilibration of samples for 24 h before gentle shaking (1 h). These were included in this study to examine aspects of water-soluble P extractions relating to DRP concentrations in overland flow. Other work in this area includes a recent Irish study by Scally *et al.* (2002) relating Morgan’s extractable soil P with simulated runoff using laboratory- and flume-scale experiments, the results of which shall be discussed later alongside some of the findings from this study.

The overall objective of this study was to attempt to relate field losses of P to laboratory extractable P taking into consideration soil sample depth, sample pre-treatment and extraction technique. Soil sample depth has been shown to affect soil P test values with higher P concentrations found at the surface 5 cm which is also assumed to be the effective depth of interaction with rainfall water (Gartley and Sims, 1994). The current study considered the effect that shallow sampling might have on the results obtained from various environmental soil P tests, including a measure of P saturation, and compared these data to the bulk soil sampled to 10 cm. The effect of soil drying and re-wetting was examined by extracting soil samples under field-moist and oven-dried conditions to gauge the effect this type of sample pre-treatment might have on water extractable P. The effect of solution-to-soil ratio on water extractable P was explored at different depths and also to simulate a range of P concentrations during soil P desorption that might be related to observed values from field measurements. Seven field sites incorporating a range of soil test P levels were used for soil P experiments, and field measurements of overland flow DRP were collected from two of these sites in an attempt to link soil extractable P with observed P losses.

2 Methodology

2.1 Soil Sampling and Preparation

Soil samples were taken from sites on the Johnstown Castle Estate. These sites had low, medium and high soil P levels determined by Morgan’s P (Morgan, 1941). The low P sites were at the Warren (Sites 1 and 2), medium P sites (5, 6 and 7) were located at the dairy and high P sites (3 and 4) at the Cowlands (Morgan’s P values to 10 cm are presented in Table 3.1).

Soil samples were collected by random sampling across each site until a minimum of 20 soil cores were collected and combined. This was repeated to obtain triplicate soil samples at each site. This procedure was used for samples removed at three different soil depths (10 cm, 5 cm and 2 cm). The 10-cm sample depth was taken using the conventional bucket sampler. For 2- and 5-cm sample depths, a soil corer was used and cores were then sliced at the required depth. All soil samples were dried overnight at 40°C, ground and sieved though a 2-mm mesh and stored at room temperature prior to analysis.

2.2 General Experimental and Statistical Procedures

Analar grade reagents were used unless stated otherwise. Stock solutions of P standards (1000 ppm P) were prepared from oven-dried KH_2PO_4, kept in cold storage (4°C) and replaced when over 1 week old. Working standards (100 ppm P) were prepared fresh daily from which a range of standard solutions was prepared. Reagents were kept in cold storage (4°C) and, where solutions were unstable, prepared fresh on day of analysis. All standards and reagents were prepared volumetrically in grade A flasks. All glass and plastic ware was washed firstly with phosphate-free detergent ‘Decon 90’, then rinsed or soaked in 10% (1 N) HCl and finally rinsed with distilled water and oven dried. All weighings were to three decimal places unless otherwise stated. Pipetting was carried out using a Ranin digital pipette. Dispensing of solutions was carried out using either grade A graduated cylinders or Eppendorf dispenser and Combitips (2.5–25 ml). Colorimetric determinations of P concentration in solutions were measured on a Cary50 UV spectrophotometer. Silica gel desiccators were employed for storage of dry materials at room temperature.

Chemical analyses were carried out in duplicate and an average value taken. Data were analysed using the statistical commands in Excel. The square of the correlation coefficient, R^2, refers to linear and non-linear correlations. The significance of R values is denoted by the symbols *, ** and *** for significance levels $p < 0.05$, $p < 0.01$, and $p < 0.001$, respectively.

2.3 Mehlich-3 P (PM3)

The Mehlich-3 method (Mehlich, 1984) was used to extract P, aluminium and iron (Mehlich, 1984) using an extractant composed of 0.2 M CH_3COOH, 0.25 M NH_4NO_3, 0.015 M NH_4F, 0.013 M HNO_3 and 0.001 M EDTA. The soil extracts were then analysed colorimetrically by ICP. The degree of P saturation was calculated from the ratio Mehlich-3 P/Mehlich-3 Al, expressed as a percentage. Phosphorus saturation is calculated depending on the type of extractant used. In this case, potential P sorption sites in soil are represented by Mehlich-3 extractable Al. Amorphous forms of Al are known to play a stronger role than Fe and other elements in P sorption and saturation and are used to describe saturation sites in soil when extracted with the Mehlich-3 reagent (Beuchemin and Simard, 1999). Phosphorus saturation is expressed as molar amounts of P already occupying sorption sites (Mehlich-3 P) relative to the number of potential P sites present (Mehlich-3 Al), and gives valuable information about P status and the potential for P sorption in soils, thereby taking into consideration aspects of soil type.

2.4 FeO Paper Strip P (Pfeo)

Iron-oxide impregnated paper strips were used as a ‘P sink’ method for estimates of labile inorganic P in soils according to the method of Menon *et al*. (1988).

2.4.1 Preparation of FeO strips

In a crystallising dish containing $FeCl_3$ solution (100 ml), filter paper circles of 12 cm diameter were immersed completely until uniformly covered with $FeCl_3$ solution.

The papers were allowed to drip dry for 2 h and then immersed in a 15% ammonium hydroxide solution until the colour change from orange to brown was complete. The papers were dried for a further 2 h before cutting into strips (10 cm × 2 cm) and stored in a cool dry cupboard before use.

2.4.2 P desorption using FeO strips (P_{feO})

Dried and sieved soil (1 g) was added to plastic bottles (100 ml) and suspended in 0.01 M $CaCl_2$ solution (40 ml). One FeO paper strip was added to each bottle and samples were shaken on an end-over-end shaker for 16 h. The strips were then removed from the bottles, rinsed with a little distilled water to dislodge any adhering soil particles and then eluted for 1 h with 0.1 M H_2SO_4 (40 ml). Phosphorus concentration in the acidic solution was determined by the ascorbic acid method.

2.5 Water Extractable P (Pw)

Water extractable P was determined using the method of Van der Paauw *et al*. (1971). Dried and sieved soil (1 g) was added to plastic centrifuge tubes and shaken with 40 ml of distilled water on an end-over-end shaker for 1 h. The solutions were centrifuged and filtered before the P concentration in solution was determined by the ascorbic acid method.

2.6 Calcium Chloride P ($Pcacl_2$)

Calcium chloride extractable P was measured using the method of Houba *et al*. (1994). Dried and sieved soil (4 g) was added to plastic bottles and shaken in 0.01 M $CaCl_2$ (40 ml) solution on an end-over-end shaker for 1 h. The solutions were centrifuged and filtered and the P concentration in solution was determined by the ascorbic acid method.

2.7 Morgan's P (Pm)

Morgan's P was measured by Johnstown Castle Laboratories using the following method (Morgan, 1941).

Morgan's extractant: 1480 ml of 40% NaOH and 1444 ml of glacial acetic acid were combined and made up to a final volume of 20 litres with distilled water. The solution pH was adjusted to 4.8. A sample of 6.5 ml of dried and sieved soil was added to 30 ml of Morgan's reagent and shaken for 30 min. The solutions were then filtered and analysed colorimetrically for P.

2.8 Colorimetric Determination of Soil Extracted P

Concentrations of P soil extracts were determined using the modified ascorbic acid method for soils according to John (1970).

2.8.1 Reagents

A stock reagent was prepared by adding the following reagents and solutions in the following order and the final volume made up to 1 litre:

ammonium molybdate solution (20 g ammonium molybdate 300 ml deionised water)
450 ml 10 N sulphuric acid
100 ml 0.5% K antimony tartrate.

A mixed reagent was prepared fresh on the day of each analysis by adding 1.5 g of ascorbic acid to 100 ml of stock reagent.

2.8.2 Standards

A 1000 ppm P stock standard was prepared by dissolving 4.3937 g KH_2PO_4 in 1 litre deionised water. A 100 ppm P working standard was prepared from this stock standard by diluting 25 ml stock standard to 250 ml. A series of standards were prepared from the working standard in the range of 0–1 ppm P in 100-ml volumetric flasks.

2.8.3 Colour development

A 5-ml aliquot of standard or sample was pipetted into a clean, dry test tube. To this was added 1 ml of mixed reagent. The solution was allowed to stand for 10 min (solution is stable for 30 min). The concentrations were measured on a UV spectrophotometer at 880 nm against a blank of distilled water.

2.9 Water-to-Soil Ratio

The effect of water-to-soil ratio on P desorption was investigated as described by the method of Yli-Halla *et al*. (1995). Duplicate soil samples were weighed to give dry soil concentrations of 4.0, 5.0, 6.25,10.0, 20.0, 200.0 g l^{-1} in a deionised water solution (water-to-soil ratios: 250–5 l kg^{-1}). The extracts were obtained and analysed for water-soluble P colorimetrically.

2.10 Field-Moist Soil Samples versus Dry Soil Samples

Fresh composite soil samples were collected at 10-cm depths from each of the Johnstown sites. Each sample was divided into two sub-samples (A and B). Sample A was air dried, ground and sieved as previously described. Sample B was hand sieved through a 2-mm mesh sieve. Duplicate 10-g quantities of each sample B were placed in clean, dry beakers and dried overnight at 40°C. The percentage moisture of each sample B was calculated after drying. Duplicate samples of both dry and wet soil were weighed out to give equivalent dry soil concentrations of 4.0, 5.0, 6.25,10.0, 20.0, 200.0 g l^{-1} in deionised water solution (solution-to-soil ratios: 250–5 l kg^{-1}). Wet soil sample weights were adjusted according to their respective moisture contents. The extracts were obtained and analysed for water-soluble P as described previously.

2.11 Field Measurements of Dissolved Reactive P in Overland Flow

Overland flow samples (500 ml) from the Upper Warren (Site 1) and the Cowlands grazed site (Site 3) were collected from runoff events from December 2001 to March 2002. Each sample was shaken, and divided into two separate samples, 1 × 50 ml and 1 × 100 ml. The 50-ml aliquot was filtered through a 0.45 µm filter and then analysed for DRP using the manual ascorbic acid method as described below. The 1 × 100-ml sample was analysed for suspended solids.

2.12 Manual Ascorbic Method for Determination of DRP in Water Samples

The following reagents were added into a clean 100-ml volumetric flask to make a combined reagent:

50 ml 5 N H_2SO_4 (70 ml of concentrated H_2SO_4 in 500 ml)

5 ml potassium antimony tartrate (1.3715 g K antimony tartrate in 500 ml deionised water)

15 ml ammonium molybdate (20 g ammonium molybdate in 500 ml deionised water)

30 ml ascorbic acid solution.

2.12.1 Standards

A 1000-ppm P stock standard was prepared by dissolving 4.3937 g KH_2PO_4 in 1 litre deionised water. A 100-ppm P working standard was prepared from this stock standard by diluting 25 ml stock standard to 250 ml. A series of standards were prepared from the working standard in the range of 0–0.8 ppm P in 100-ml volumetric flasks.

2.12.2 Colour development

A 5-ml aliquot of standard or water sample was pipetted into a clean, dry test tube. To this was added 1 ml of Combined reagent. The solution was allowed to stand for 10 min (solution is stable for 30 min). The concentrations were measured on a UV spectrophotometer at 880 nm against a blank of distilled water.

2.13 Suspended Solids (SS)

Whatman GF/C glass microfibre filters (47 mm) were rinsed with 50 ml distilled water and dried at 104°C for 4 h. Each filter was allowed to cool and was then weighed. Each 100-ml aliquot of overland flow collected from above was filtered through individual pre-prepared filters under vacuum. The filters were retained and oven dried at 104°C for 2 h (or until the weights were consistent). The filtrates were discarded. Each filter was allowed to cool and was then re-weighed to determine the suspended solids concentration in mg l^{-1} by subtraction. All weights were taken using a Sartorius balance with an accuracy of 0.1 mg.

3 Results and Discussion

3.1 Sample Depth and Extracting Solution

Soil samples at 2, 5 and 10 cm were taken in triplicate at each site in June 2001 and were extracted using the following P tests: Mehlich-3, Morgan's P, iron-oxide paper strip, water-soluble P and calcium chloride. The results for triplicate samples were averaged for each depth and are presented for each site in Table 3.1. In some cases soil P varied with depth with more notable differences between samples taken at 2 cm and 10 cm. However, these differences were not consistent across all soil tests and sites. Statistical analysis (ANOVA) was carried out on data from soil samples taken in triplicate at each sample depth and analysed for Pfeo, Pw, Pcacl$_2$ and Pm. Statistically significant differences were not consistent at all sites and sample depths , possibly due to spatial variability within and between sites. These results are presented in Appendix A.

The tests employed extracted varying amounts of P – Mehlich-3 and iron-oxide paper strip tests extracted the highest amounts and calcium chloride extracted the least. Morgan's P and water-soluble P were comparable in the ranges of concentrations extracted from each site. These results are also presented in Table 3.1.

3.2 Water-to-Soil Ratio

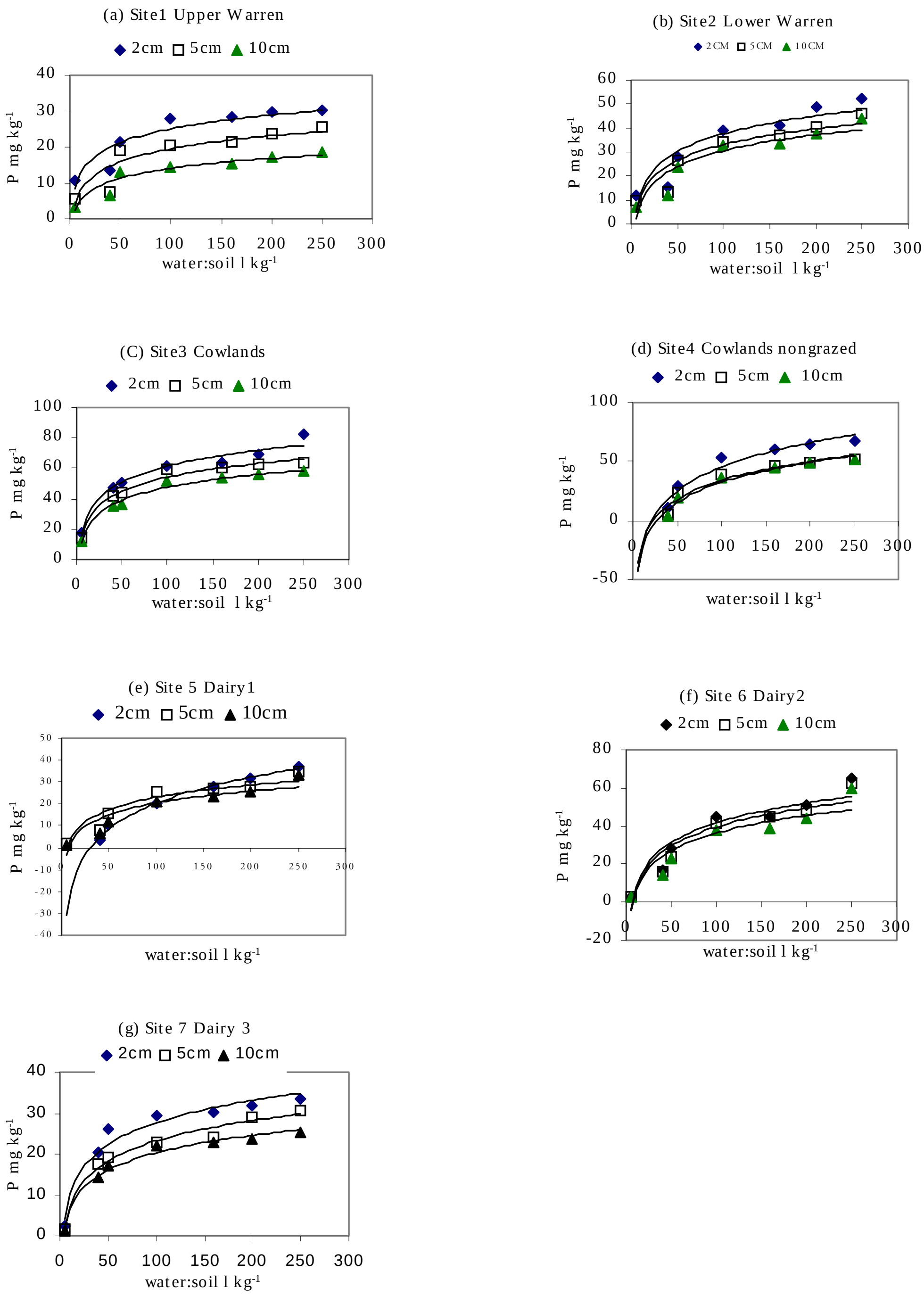
The effect of varying the water-to-soil ratio was explored using the water-soluble P test, widening the water-to-soil ratio from 5 to 250 l kg^{-1}. The effect of water-to-soil ratio

Table 3.1. Soil P extraction data and % P saturation at 2, 5 and 10 cm sample depths for each site.

Site	Depth (cm)	PM3	Pfeo	Pw (mg kg^{-1})	Pm	Pcacl$_2$	Psat (%)
1	2	63	26	12.3	7.0	2.1	8.6
	5	30	19	7.6	4.2	1.0	3.8
	10	38	18	6.7	3.1	0.8	4.3
2	2	76	44	15.7	8.0	1.4	9.8
	5	82	37	13.8	8.7	1.2	9.5
	10	75	38	11.7	6.9	0.9	8.7
3	2	129	102	47.7	35.7	8.8	20
	5	121	99	43.7	27.2	6.0	17.1
	10	124	82	36.0	20.6	4.7	16.3
4	2	157	100	53.2	29.4	10.0	20.8
	5	140	78	38.8	24.5	5.9	18.5
	10	135	77	36.8	21.0	5.1	17.4
5	2	50	33	10.1	7.8	2.8	6.6
	5	40	24	8.3	5.7	2.5	5.4
	10	29	22	6.9	4.1	1.7	3.9
6	2	95	48	16.6	11.5	2.9	10.5
	5	84	44	14.5	9.7	2.5	9.6
	10	87	41	15.9	8.3	2.3	9.4
7	2	64	37	20.3	10	3.3	8.1
	5	59	37	17.4	8.3	1.9	6.9
	10	64	32	14.1	6.8	1.2	7.3

on P desorption is presented in the log plots in Fig. 3.1 for each of the field sites and at each sample depth 2, 5 and 10 cm. The total quantity of desorbed P from a kilogram of soil increased strongly with increasing water-to-soil ratio. This occurred for each soil and at each depth with highly significant correlations between these two variables.

The highest water-to-soil ratio (250 l kg^{-1}) extracted the highest amounts of desorbable P and amounts extracted from samples taken at 2 cm exceeded those at lower depths of 5 and 10 cm from each site. Values of desorbable P at the highest water-to-soil ratio (Pw$_{250}$ mg kg^{-1}) were plotted against the degree of P saturation (% Psat) for each sample depth (Fig. 3.2). The positive


(a) Site1 Upper Warren

(b) Site2 Lower Warren

(C) Site3 Cowlands

(d) Site4 Cowlands nongrazed

(e) Site 5 Dairy1

(f) Site 6 Dairy2

(g) Site 7 Dairy 3

Fig. 3.1. Log plots of water extractable P against water-to-soil ratios at 2, 5 and 10 cm for each site where R^2 values > 0.82 and p > 0.001 at each site.

correlation between these two parameters indicates that high levels of P saturation at high soil test P gave greater quantities of desorbed P to water. However, whilst the degree of P saturation and amounts of P desorbed were greater at the shallow sampling depth of 2 cm compared to 10 cm, the degree of correlation between these two variables was greater at 10 cm than at 2 cm. This suggests that either the sampling error is greater at 2 cm than at 10 cm, or the measurement of % Psat is more accurate at 10 cm since the bulk of soil at this depth gives a better reflection of saturation or sorption sites represented by Al.

At the seven sites in this study, the percentage organic matter (%OM) (Appendix B) was higher at the surface 2 cm compared to values measured to 10 cm (t = 4.26***) and amounts of Mehlich-3 Al were lower at the surface 2 cm compared with values measured to 10 cm (t = 3.10*). In addition, the %OM correlated negatively with the amounts of Mehlich-3 extractable Al (R^2 = 0.49***) and this relationship is presented in Fig. 3.3. In a recent study by Daly *et al.* (2001), organic matter inhibited P sorption and desorption, particularly in high organic matter soils, by blocking sorption sites for P. The negative relationship between %OM and Mehlich-3 Al suggests that as organic matter in soils increases amounts of Mehlich-3 Al decrease, indicating that most of the sorption or saturation sites for P are located below the surface where less organic matter accumulates. In terms of environmental losses of soil P, the 10-cm sample depth may provide a better indication of P saturation and potential losses to water than shallower sampling depths.

3.3 Sample Pre-Treatment

The effect of drying and re-wetting of soil on water extractable P was investigated on samples taken at 10 cm depth from each of the seven sites in November 2001. Kurz (2000) found elevated DRP concentrations in overland flow from samples taken directly after periods of dryness. This has been attributed to microbial P release upon re-wetting of dried soil. To investigate this effect under laboratory conditions, soil samples were extracted with the range of water-to-soil ratios outlined in the previous section under oven-dried (40°C) and field-moist conditions for comparison. Oven-dried samples gave higher amounts of extractable P than field-moist samples (Fig. 3.4). Over the range of water-to-soil ratios used, water-soluble P increased after drying by 110–560% from soils taken at six of the seven sites. The exception to this trend was seen at Site 1, the lowest P soil, and is likely due to analytical error since Kurz (2000) observed pronounced DRP concentrations at this site in overland flow following periods of dryness. Turner and Haygarth (2001) have also reported increases in soluble P after drying at 30°C for 1–3 days and have attributed this increase to the solubilisation of organic P released from microbial cells following cell rupture and osmotic shock due to rapid rehydration of dried soils. The authors correlated the increase in extractable P with amounts of microbial P (R^2 = 0.58) to illustrate the connection between microbial P release and solubilisation of organic P. However, in the present study, the increase in water-

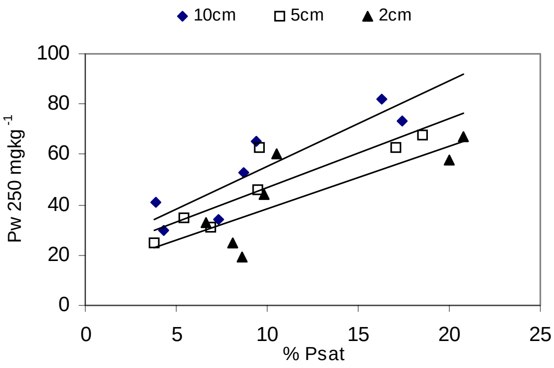


Fig. 3.2. Extractable P at the highest water-to-soil ratio (250 l kg^{-1}) plotted against % P saturation at 2- (R^2 = 0.61*), 5- (R^2 = 0.79) and 10-cm (R^2 = 0.81**) sample depths for each site.**

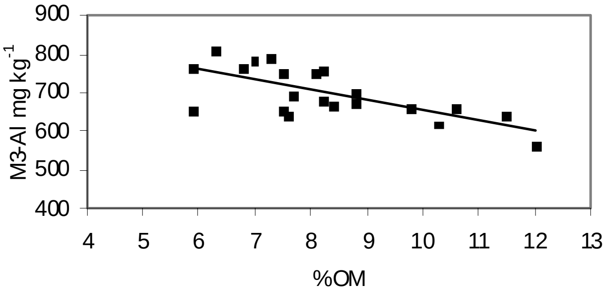


Fig. 3.3. The relationship between Mehlich-3 extractable Al (M3-Al) and percentage organic matter (%OM) in soils sampled at 2, 5 and 10 cm from seven sites; y = –26.5x + 917, R^2 = 0.49*.**

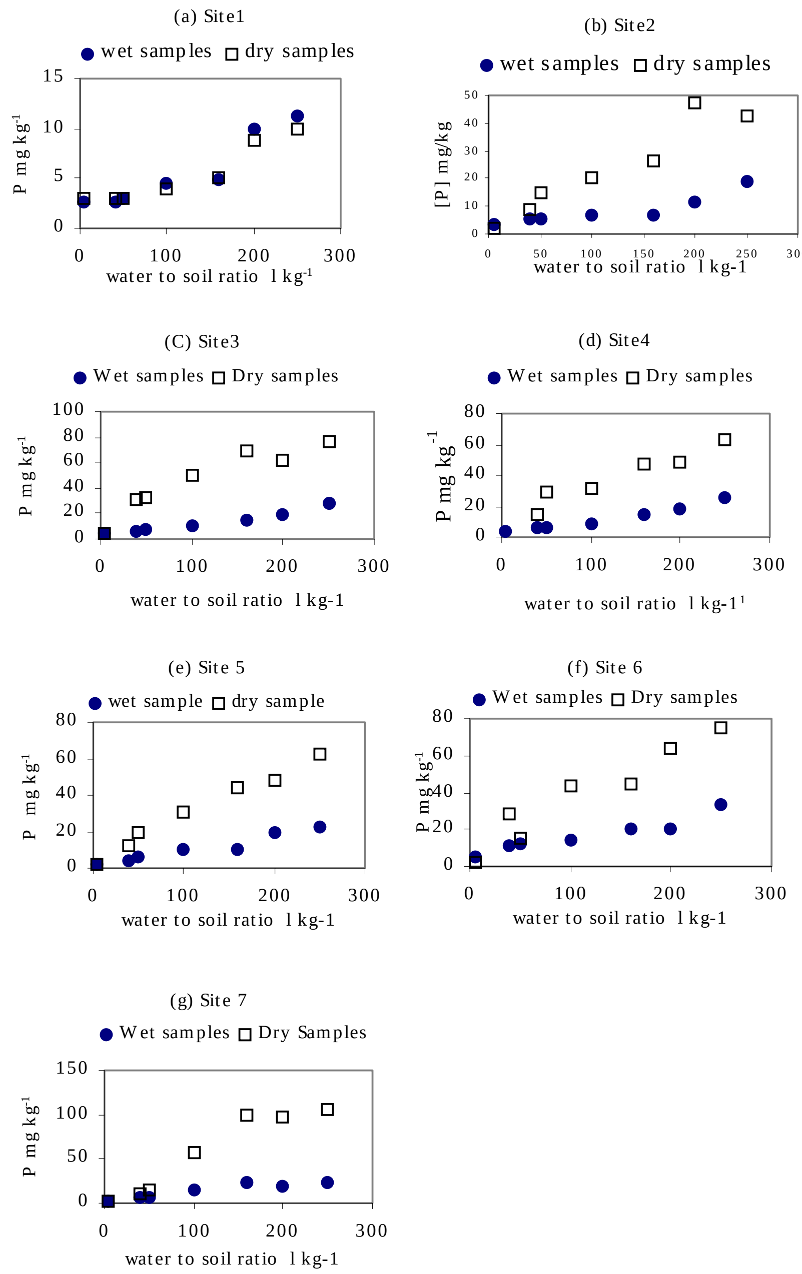


Fig. 3.4. Water extractable P at a water-to-soil ratio of 5–250 l kg^{-1} on field-moist and oven-dried samples at 10 cm for each site.

soluble P due to drying at 40°C responded to water-to-soil ratios (Fig. 3.5). The effect of widening water-to-soil ratios usually encourages more desorbable P from the soil solid phase into solution. The relationship between the two variables in Fig. 3.5 indicates that as water-to-soil ratios were widened the increase in soluble P due to drying and re-wetting also increased. Drying soil to 40°C may have rendered some unavailable organic or inorganic forms of P more readily desorbable, hence the response to changes in water-to-soil ratios. This suggests that microbial P release is only one explanation for the observed changes and that some chemical processes are also involved.

3.4 Soil Analyses versus Field Measurements

Field Sites 1 (Warren) and 3 (Cowlands) were instrumented for overland flow collection. Overland flow

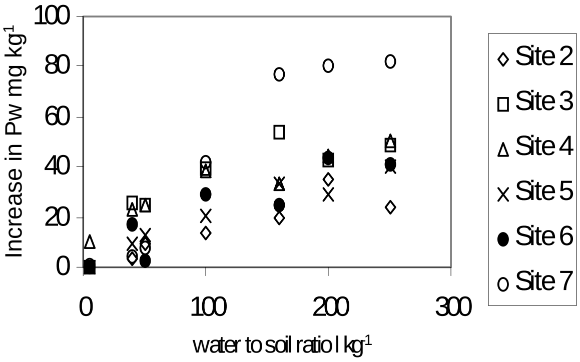


Fig. 3.5. Increase in water extractable P against the water-to-soil ratio for each site.

samples from events at these sites were collected from December 2001 to March 2002 and analysed for DRP and SS. Soil samples to 10 cm were collected during the same time period and extracted for water-soluble P over a range of water-to-soil ratios (5–250 l kg^{-1}). The event dates and summary statistics of DRP and SS are presented in Table 3.2 for the two sites. Average DRP concentrations from events at Site 1 ranged from 0.032 to 0.067 mg l^{-1} compared to higher values at Site 3 of 0.261–0.620 mg l^{-1}, reflecting the differences in soil P levels between the sites. The average concentrations of SS from events were also higher at Site 3 than at Site 1, with values ranging from 29 to 43 and from 9 to 28 mg l^{-1} for Sites 3 and 1, respectively.

The P load or loss from each site was calculated using total flow volumes and mean DRP concentrations from events. These were summed over the 3-month sampling period to give an export rate expressed on a per-hectare basis. Site 1 lost 0.065 kg P ha^{-1} from December to March compared to 0.457 kg P ha^{-1} from Site 3, representing a 7-fold difference in P loss between the sites. These figures were scaled up into yearly export rates of 0.26 and 1.83 kg P ha^{-1} year^{-1} from Sites 1 and 3, respectively. Kurz (2000) recorded yearly losses of 0.698 and 4.764 kg P ha^{-1} year^{-1} during 1997 for Sites 1 and 3, respectively, noting that 41% of total exports at both sites occurred during an exceptionally high rainfall event between 3rd and 10th August 1997. This may account for the comparatively lower estimates calculated in this study although a 7-fold difference between the two sites remains.

Suspended solids data were also calculated as yearly export rates using total flow and mean concentrations for each event. Whilst concentrations of SS were comparatively higher at Site 3, when these data were expressed as kg ha^{-1} both sites appeared to lose similar loads of SS during events over the 3-month period.

3.4.1 DRP concentrations during events

The profiles of events for the two sites are presented in Figs 3.6 and 3.7 for Sites 3 and 1, respectively. The flow rates (l s^{-1}) are plotted alongside DRP values for each sample collected during the events. The dates in the chart titles represent the duration of the event as defined by flow data and dates in the x-axis correspond to dates on which water samples were collected. At Site 3 DRP

Table 3.2. Event dates and summary statistics of DRP and SS for Sites 3 and 1.

Event duration	Event no.	No. samples	Flow l	DRP (mg l^{-1})		P load (kg P ha^{-1})	SS (mg l^{-1})		SS load (kg ha^{-1})
				Range	Mean		Range	Mean	
Site 3									
3.12.01–6.12.01	1	47	26,259	0.356–0.730	0.620	0.035	1–393	33	1.88
13.01.02–12.02.02	3	151	413,376	0.037–0.695	0.411	0.37	0–184	29	26.10
25.02.02–25.02.02	4	6	3,832	0.207–0.312	0.261	0.002	32–50	43	0.36
28.02.02–2.03.02	5	23	56,064	0.334–0.506	0.417	0.05	10–107	39	4.75
Site 1									
3.12.01–5.12.01	1	16	180,394	0.025–0.085	0.059	0.008	2–85	20	2.34
06.01.02–13.12.02	2	3	42,949	0.027–0.069	0.046	0.001	4–14	9	0.25
13.02.02–13.02.02	3	77	1179,019	0.001–0.211	0.067	0.050	1–125	28	21.44
24.02.02–2.03.02	4	20	281,189	0.004–0.084	0.032	0.006	2–73	17	3.10

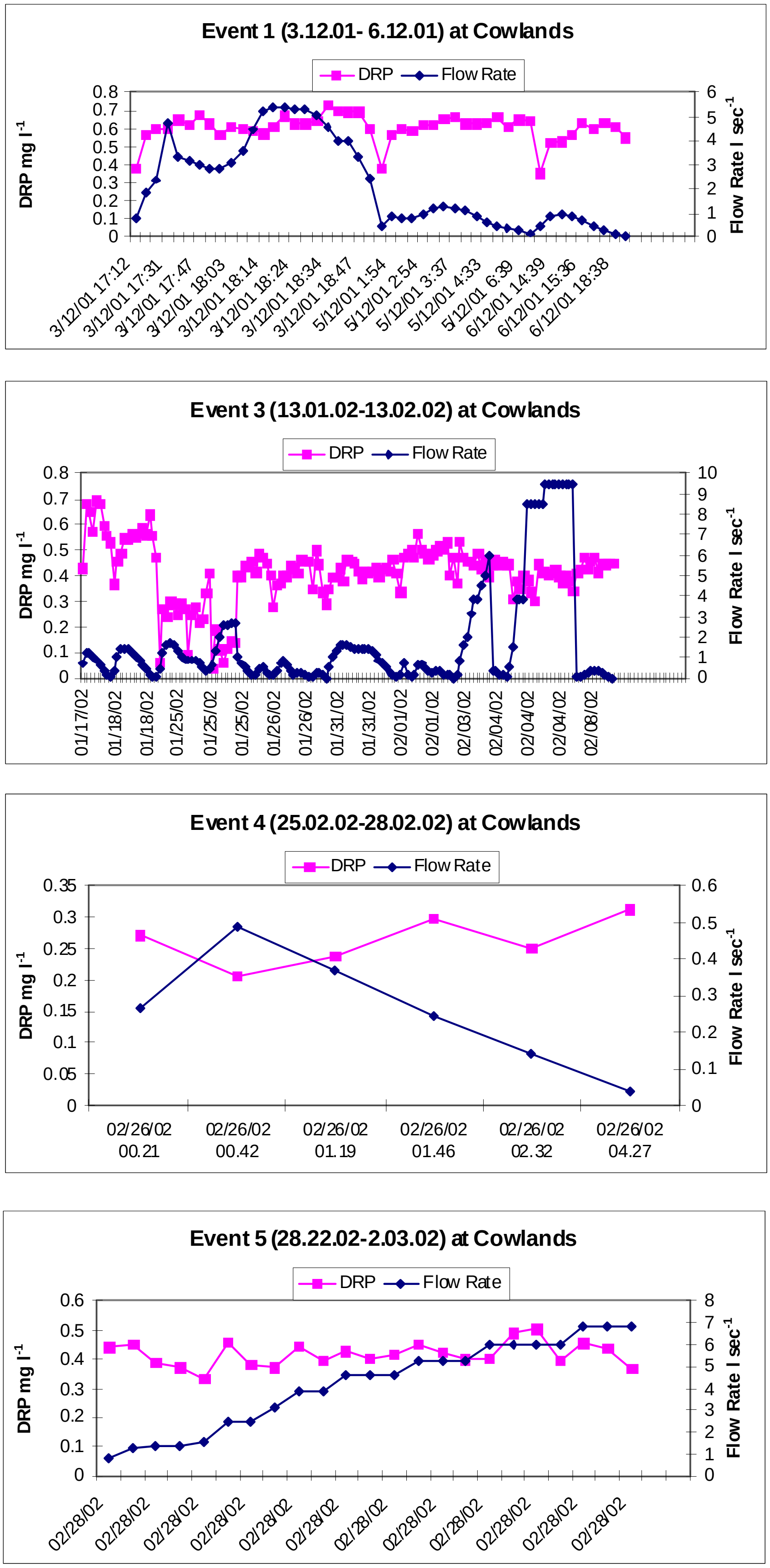


Fig. 3.6. Event profiles of DRP and flow rate at Site 3.

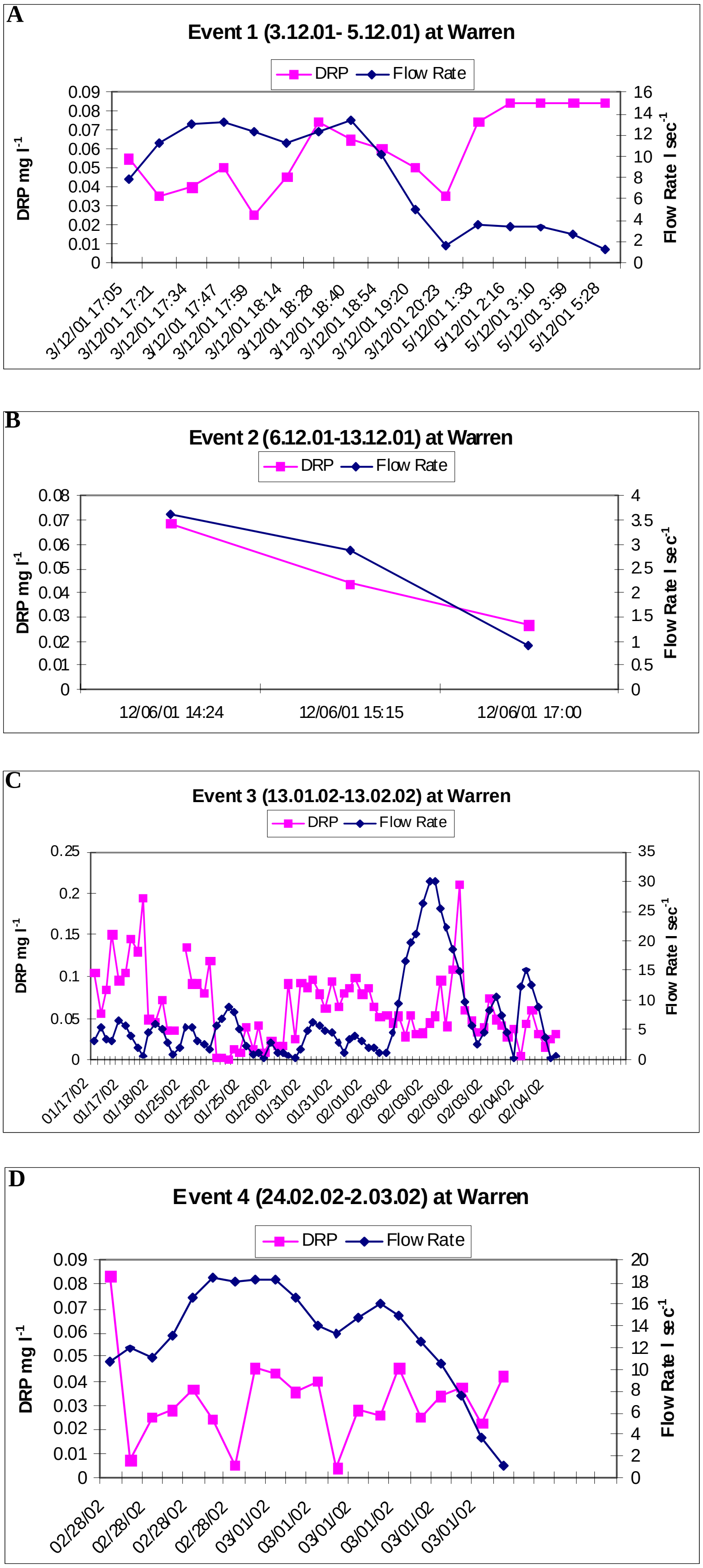


Fig. 3.7. Event profiles of DRP and flow rate at Site 1.

values appear to plateau, particularly in event 3 (17.01.02–12.02.02) where, after an initial rise and fall, DRP values level off and continue to plateau towards the end of the event. The corresponding event at Site 1 (event 3, 13.01.02–13.02.02) is presented in Fig. 3.7 (C) and values of DRP do not appear to plateau towards the end of the event as observed at Site 3. This event captured 67% and 66% of samples collected at Sites 3 and 1, respectively, from December 2001 to March 2002, and most of the soil sampling dates fell within this time frame.

3.4.2 Relating SS to DRP

Samples of overland flow collected from the two sites were measured for DRP and SS to ascertain if a relationship between SS and DRP exists. Values of SS below 10 mg l^{-1} have been filtered out of the data at both sites since lowest recorded values of SS are 8 mg l^{-1} with an accuracy of ±15%. The relationship between DRP and SS at the high P site (Site 3) is depicted in Fig. 3.8(a) and indicates that as SS increased DRP values in overland flow also increased. Although the relationship between the two variables is weak (R^2 = 0.18), it is significant ($p < 0.001$). This suggests that since the soil at Site 3 is saturated with P at the surface, SS from this site may also have contributed to DRP in overland flow. However, at Site 1, the low P site, the relationship between SS and DRP was similar in magnitude and significance but in the opposite direction, i.e. as SS increased, DRP values decreased (Fig. 3.8(b)). This suggests that soil eroded from this site is deficient in P and may have re-absorbed some P from solution. Another possible explanation for the reverse trend in SS and DRP at the low P site may be considered when SS (mg l^{-1}) is converted to water-to-soil (or rather water-to-SS) ratio (l kg^{-1}) by inverting SS data. The relationship between these two variables is plotted in Fig. 3.8(c) and shows that as water-to-SS ratios were widened, DRP in solution increased. This suggests that during overland flow, soil particles were mixed with overland flow water and desorption of P occurred as water-to-soil ratios widened during the event. Perhaps this effect was captured at the low P site because soil at the surface was not heavily saturated with P compared to the high P site.

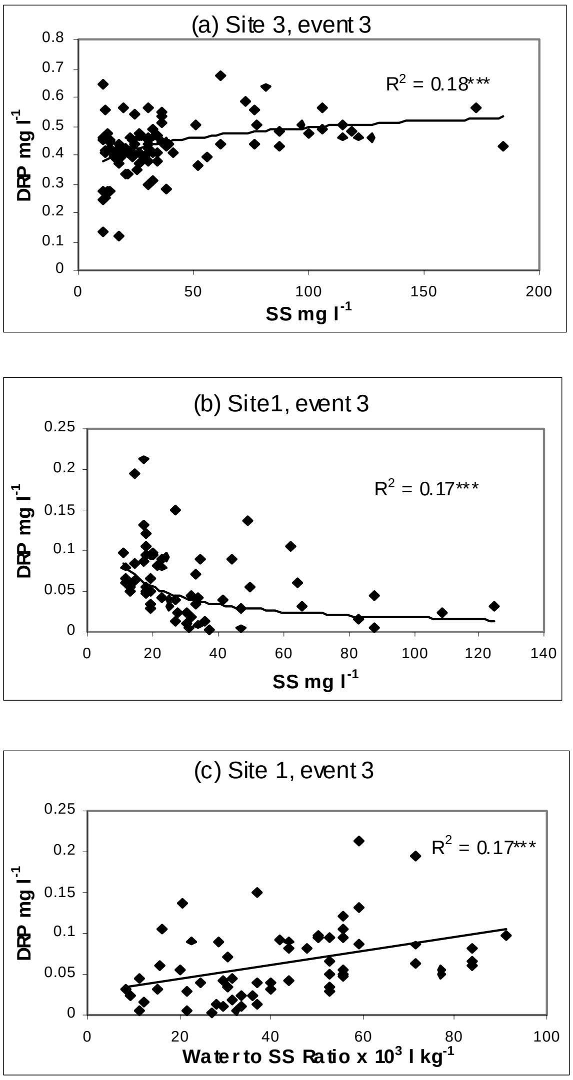


Fig. 3.8. Relationship between DRP in overland flow and (a) water-to-SS ratio at Site 1 during event 3, (b) water-to-SS ratio at Site 3 during event 3 and (c) SS at Site 3 during event 3.

3.4.3 Relating soil solution P to DRP concentrations

Previously, quantities of P (mg kg^{-1}) were plotted against a water-to-soil ratio to illustrate the desorption effect. However, to compare laboratory analyses with field measurements the actual concentrations in solution (mg l^{-1}) were used. Concentrations of water-soluble soil P in soil sampled during the runoff events were compared with concentrations of overland flow DRP. Runoff events at Site 3 were characterised by plateau concentrations during and at the end of events, particularly during event 3, where DRP values levelled off at three stages over the event. The data during event 3 were averaged at these stages to give plateau DRP values, and for other events at Site 3 an average value of DRP was taken. The data from soil samples taken during events at Site 3 are represented as concentrations of water-soluble P in solution, plotted against water-to-soil ratios (Fig. 3.9). Plateau values of DRP in runoff were used to find corresponding water-to-soil ratios from the plots to calculate a value of extractable P (mg kg^{-1}). These data are summarised in Table 3.3.

At Site 3, values of DRP corresponded to concentrations found in soil-water extracts in the laboratory data, with DRP values ranging from 0.208 to 0.620 mg l^{-1} and reflected in water-to-soil ratios from 5 to 250 l kg^{-1}. The corresponding quantities of extractable P from soil ranged from 3.1 to 52.2 mg kg^{-1}. If the observed DRP values presuppose an effective extraction ratio of 5–250 l kg^{-1}, the equivalent SS would be 4000–10,000 mg l^{-1}. However, the observed values of SS were of a significantly lower magnitude (29–43 mg l^{-1}). Whilst SS accounted for some variation in DRP values (Fig. 3.8), the extraction ratio experiments reveal that a substantial part of the DRP originates from the bulk of the soil in the field. Yli-Halla *et al*. (1995) calculated that SS accounted for 16–38% of DRP in surface runoff from a high soil P site (Pw_{50} = 19 mg kg^{-1}) and that observed DRP concentrations fell within the range of water-soluble P extracts extracted at a water-to-soil ratio between 100 and 250 l kg^{-1}. The Cowlands is a comparatively high soil P site (Pw_{50} = 23 mg kg^{-1}) and observed DRP values in surface runoff presuppose a water-to-soil ratio of 5–250 l kg^{-1}, with SS accounting for 17% of the variation in DRP values.

At Site 1 (low P level), the results from soil extraction at a water-to-soil ratio of 5–250 l kg^{-1} did not reflect the observed DRP values in runoff samples (Fig. 3.10). Average values of water-soluble P concentrations ranged from 0.129 to 0.749 mg l^{-1} over a water-to-soil ratio range of 250–5 l kg^{-1}. The minimum values ranged from 0.072 to 0.385 mg l^{-1}, from soils extracted at 5–250 l kg^{-1}. Concentrations of DRP measured in runoff samples ranged from 0.001 mg l^{-1} to 0.214 mg l^{-1} over all events and the average value over the monitoring season was 0.05 mg l^{-1}, which was slightly lower than the minimum concentration found in soil extracts at a water-to-soil ratio of 200–250 l kg^{-1} (0.072–0.08 mg l^{-1}). Average SS (18.5 mg l^{-1}) corresponded to a water-to-soil ratio of 54,054 l kg $^{-1}$, too high to sustain observed DRP concentrations in runoff.

3.4.4 Relating losses to water-to-soil extractable P

Losses to water from Sites 1 and 3 have been compared with Morgan's P concentrations, and the 7-fold difference in export rates between the sites is often quoted as an indication of potential loss from soils at low (Site 1) and high P (Site 3) levels (Tunney *et al.*, 2000). In addition, Kurz (2000) found that despite the variations in flow volume between the sites, the increase in soil P levels from Site 1 to Site 3 was responsible for the same trend in P export.

In this work, soil samples from Sites 1 and 3 were analysed using five different soil P tests giving concentrations (mg P kg^{-1}) of extractable P (Table 3.1). For Sites 1 and 3, these data were converted to kg P ha^{-1} on a mass basis using the bulk density and sample depth of 10 cm so that the relative difference in extractable soil P might be compared with the relative difference in export rates (kg P ha^{-1} year^{-1}).

Most soil P data are expressed in mg P kg^{-1} soil (Sharpley *et al.*, 1994) but quoting soil P data on a volume basis either as mg l^{-1} or kg ha^{-1} considers differences in bulk

Table 3.3. Plateau values of DRP from events at Site 3 with the corresponding water-to-soil ratio taken from water-soluble P extraction and calculated extractable P mg kg^{-1}.

Event dates	DRP (mg l^{-1})	Water-to-soil ratio (l kg^{-1})	Pw (mg kg^{-1})
3.12.01 – 6.12.01	0.620	5	3.1
13.01.02–12.02.02	0.558, 0.208, 0.427	40, 250, 86	22.3, 52, 36.7
25.02.02–25.02.02	0.261	200	52.2
28.02.02–2.03.02	0.417	40	16.7

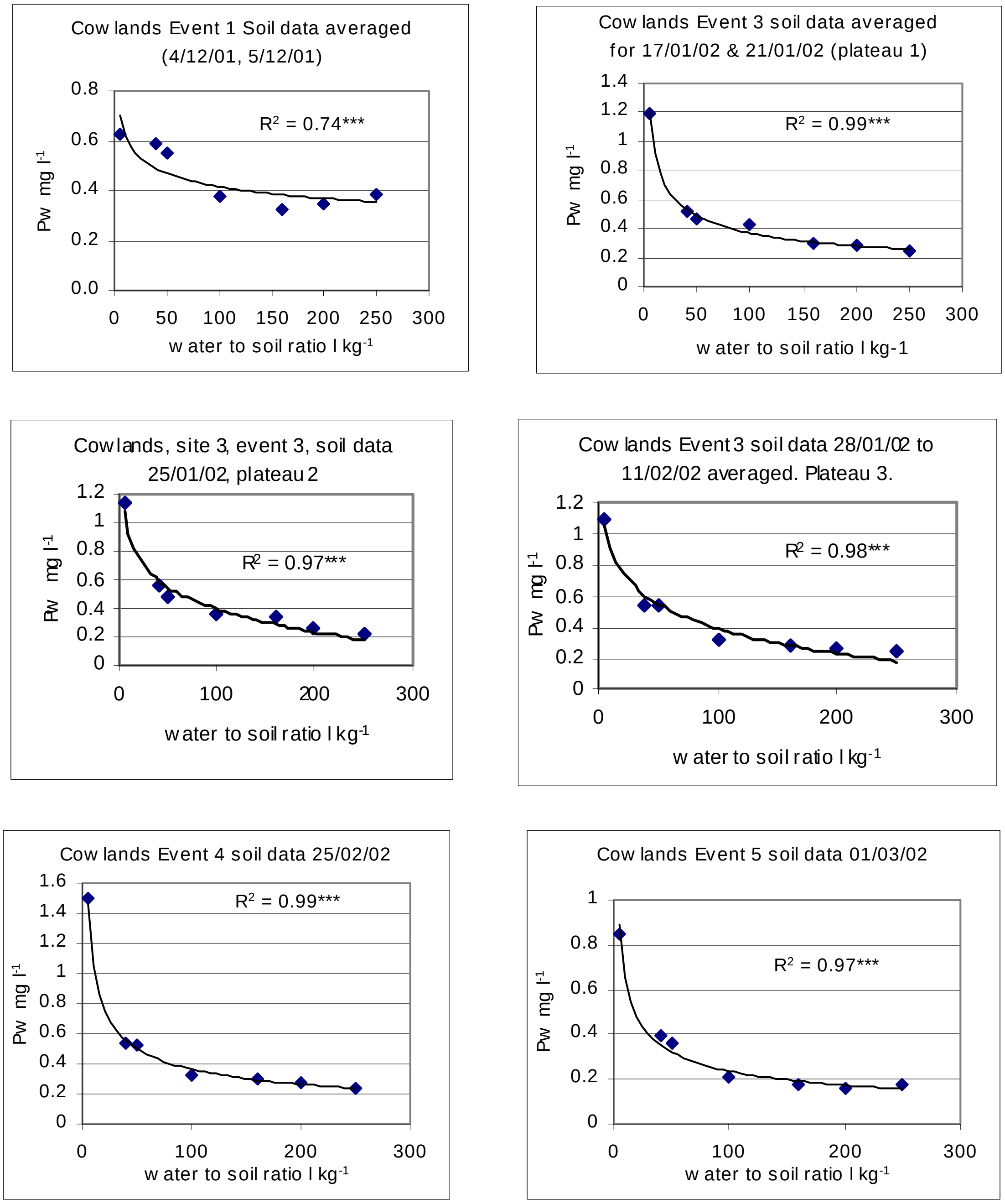


Fig. 3.9. Soil extractable water-soluble P concentrations at water-to-soil ratios of 5–250 l kg^{-1} from samples taken at 10 cm during overland flow events at Site 3.

density between soil types. Even if bulk density is not measured directly, reliable estimates can be calculated from percentage organic matter. By taking cognisance of differences in soil type, soil P data quoted on a volume basis have explained some variations in soil P desorption in other studies (Daly *et al.*, 2001). Phosphorus export rates from fields were compared against soil P data on a volume basis in this study.

Water extractable Pw_{40} (i.e. the standard Pw that uses a water-to-soil ratio of 40) from samples taken on different dates were converted to kg P ha^{-1} and compared (Table 3.4). The average Pw_{40} from samples taken during the overland flow period (December 2001 to March 2002) was lower than values measured from samples taken the previous June and November 2001, possibly due to spatial and temporal variation in soil biology or

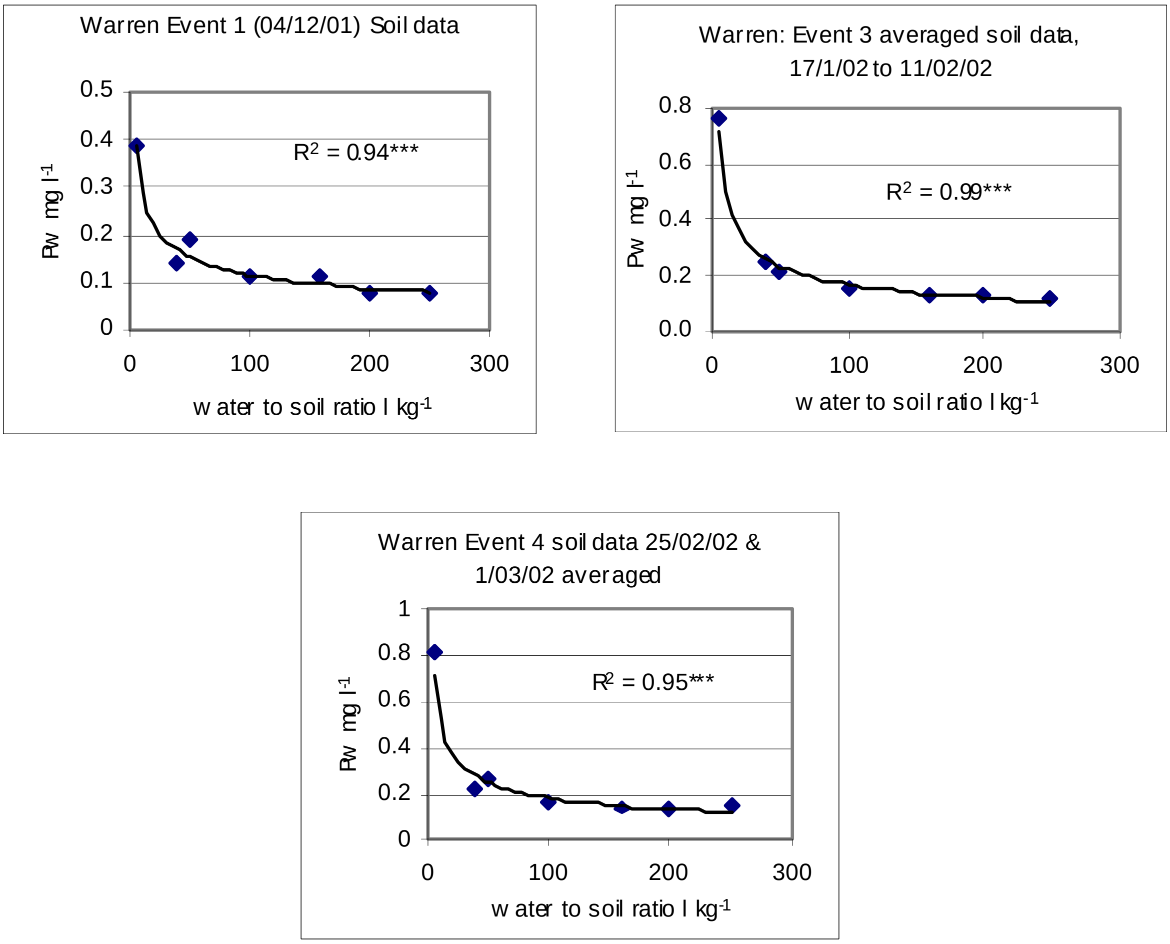


Fig. 3.10. Soil extractable water-soluble P data at water-to-soil ratios of 5–250 l kg^{-1} from soil samples taken at 10 cm during events at Site 1.

Table 3.4. Water extractable P at a water-to-soil ratio of 40 l kg^{-1} from soil samples taken from June 2001 to March 2002.

Site	Pw_{40} measured from soils samples taken June 2001 (kg P ha^{-1})	Pw_{40} measured from soil samples taken November 2001 (kg P ha^{-1})	Pw_{40} measured from soil samples taken from December 2001 to March 2002 (kg P ha^{-1})
3	3.03	2.68	1.83
1	0.61	0.27	0.82
Ratio	4.9	9.9	2.2

chemistry. However, these results were combined to give an average value of Pw_{40} and compared against other soil P tests (expressed as kg P ha^{-1}).

Soil P data were compared alongside export rates taken from this study and those measured in 1997 by Kurz (2000), in terms of the relative difference between the two sites by calculating a ratio of P loss and extractable P (Table 3.5). The ratio of P loss between Sites 1 and 3 estimated in this work compared well with previous work (Kurz, 2000) and in general there was a 7-fold difference in P export between the sites.

The ratio of soil extractable P between sites varied depending on test employed. The lowest differences between sites was observed using Mehlich-3 and the

Table 3.5. Phosphorus export rates from Sites 1 and 3 and soil extractable P on a mass basis.

Site	P export rate December 2001 to March 2002	Estimate of yearly estimate 2001–2002	Yearly export rate 1997 (Kurz, 2000)	Soil extractable P expressed on a mass basis (kg P ha^{-1})				
	(kg P ha^{-1} DRP)	**(kg P ha^{-1} year^{-1} DRP)**		**PM3**	**Pfeo**	**Pw**	**Pm**	**Pcacl$_2$**
3	0.457	1.83	4.764	10.51	6.97	2.51	1.75	0.40
1	0.065	0.26	0.698	3.48	1.66	0.56	0.28	0.07
Ratio	7	7	6.8	3.0	4.2	4.5	6.2	5.5

highest ratio was observed using Morgan’s P. The relative difference in P extractability using Morgan’s P data was closer to the difference in export rates, compared with other soil P tests. Using the 2001–2002 monitoring data, the yearly export rate of P loss from Sites 3 and 1 was estimated as 1.83 and 0.26 kg P ha^{-1} year^{-1}, respectively. These values are comparatively close to Morgan’s P expressed on a mass basis with values of 1.75 and 0.28 kg P ha^{-1} measured for Sites 3 and 1, respectively.

4 Conclusions

The results from the soil and water analyses carried out in this work make some important points with regard to soil P testing and the implications for an environmental soil P test. Firstly, the issue of soil sample depth has been examined with the use of various extraction methods on the seven sites and at various water-to-soil ratios. The results shown in Table 3.1 represent an average of three soil samples taken at each depth. The lack of a consistent statistical difference in P extracted between samples taken at 2, 5 and 10 cm perhaps illustrates the effect of spatial variation among triplicates or possibly the errors involved in sampling to shallow depths of 2 cm (Appendix A). To justify a change in soil sample depth for an environmental soil P test, a consistent statistical difference between soil P at different depths would need to exist so that some empirical relationship between conventional agronomic testing to 10 cm and an environmental test to a shallower depth could be established. Otherwise, an agronomic soil P test could not be related or converted to an environmental indicator. The recent work by Scally *et al.* (2002) suggested the adoption of soil sampling to 2 cm based on a correlation ($n = 6$) between Morgan's P from soil sampled to 2 cm and DRP sampled from a beaker containing 500 ml of water placed on the surface of soil cores sampled to 6 cm. However, it is not clear whether the authors considered spatial variation and have suggested the adoption of a 2-cm sample depth for Morgan's P without relating the results to actual field losses.

Percentage P saturation in soils at the three depths was correlated with water-soluble P extracted at the widest water-to-soil ratio of 250 l kg^{-1}. The relationship and its significance between these two variables improved with sample depth, particularly, between 2 cm ($R^2 = 0.61^*$) and 10 cm ($R^2 = 0.81^{**}$). Furthermore, higher amounts of organic matter at the surface 2 cm compared to 10 cm were negatively correlated with amounts of extractable Al, indicating that P sorption may be inhibited at the surface and that samples taken to 10 cm present a more accurate reflection of the degree of P saturation within the soil matrix and hence potential losses to water. The %Psat measurement represents the amount of P in soil relative to the number of sorption sites available for saturation and is often used as an environmental indicator (Beauchemin and Simard, 1999) since it considers sorption potential as a feature of soil type. That the R^2 value increased with sample depth suggests that soil sampled to 10 cm captured the bulk of soil and potential sorption and saturation sites that may contribute to water-soluble P.

In terms of edge-of-field losses, SS accounted for 18% of the variation in DRP collected in overland flow samples from the high P site. This indicates that most of the P in overland flow samples probably comes from the bulk of the soil as opposed to soil particles at the surface which contribute a small amount. In terms of soil sample depth, the conventional depth of 10 cm captures the bulk of the soil and may be a better representation of soil P saturation and potential P released to overland flow than shallower sample depths to 2 and 5 cm.

Relating soil P analyses to field measurements of P in overland flow from Sites 1 and 3 has indicated that DRP concentrations observed in overland flow were reproduced at water-to-soil ratios between 5 and 250 l kg^{-1} at the high soil P site only. To compare laboratory extractable soil P with overland flow P data from both sites, all of the soil test P data for both sites were expressed on a mass basis (kg P ha^{-1}) and compared with export rates of P in overland flow. The relative difference in DRP export rates between the two sites was compared against the relative difference in extractable P on a mass basis for soil sampled to 10 cm taken from the sites. The ratio of Morgan's P was more comparable to the ratio of the export rates than other soil P tests in this instance.

In this study, Morgan's P data from Sites 1 and 3 were more comparable to DRP loss in overland flow from the sites than the other soil P tests. This conclusion is based on 3 months of overland flow data extrapolated to an annual export rate and soil samples taken in triplicate from the previous summer and during the overland flow period, December to March. Thus, as it stands, Morgan's P, the standard agronomic test, taken to 10 cm depth, provided the best indicator of P loss for the two sites investigated in this work.

The data presented in this work have uncovered some interesting environmental aspects of soil P testing. Spatial variation, drying and re-wetting of soils and the effect of widening water-to-soil ratios have been shown to affect soil P results in an environmental context. In addition, the role of SS has been investigated and found to account for only 18% of the variation in DRP concentrations at the high P site, with most of the soluble P assumed to come from the bulk of the soil at a deeper depth than 2 cm.

Further research in this area has been initiated with the recruitment of an M.Sc. student under the Teagasc Walsh Fellowship scheme, to investigate the effects of drying and re-wetting of soils on water-soluble P and P in overland flow. This new work will link in with existing post-graduate studies co-funded under the RTDI programme investigating the effects of flow on P loss in flume- and column-scale experiments and the effect of grazing animals on P loss.

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Appendix A

ANOVA for soil P data (Pfeo, Pw, Pcacl$_2$ and Pm) from samples taken in triplicate at 2-, 5- and 10-cm depths with F-test results (F-ratio and significance) showing inconsistent differences in P data between sample depths and sites. Significance levels p = 0.5, 0.1 and 0.001 are denoted by the symbols *, ** and *, respectively, whilst n/s denotes not significant at the 0.05 level.**

Site no.	P-test	Sample depth			F-ratio
		2 cm	5 cm	10 cm	
1	Pfeo	35	17	18.2	F = 3.11, n/s
	mg kg^{-1}	22	19	18.0	
		22	20.4	18.4	
	Pw	11.8	5.4	6.2	F = 11.75**
	mg kg^{-1}	12.4	8	7.2	
		16.4	9.4	6.6	
	Pcacl$_2$	1.8	0.8	0.75	F = 15.74**
	mg kg^{-1}	1.85	1.05	0.8	
		2.65	1.15	0.95	
	Pm	7.1	3.4	2.8	F = 5.43*
	mg l^{-1}	4.4	3.6	2.6	
		4.3	3.6	3.1	
2	Pfeo	43	44.45	42.1	F = 1.59, n/s
	mg kg^{-1}	48.35	32.55	34.3	
		39.9	34.1	37.1	
	Pw	14.1	13.1	10.85	F = 4.19, n/s
	mg kg^{-1}	16.05	13.85	11.75	
		16.85	18.15	12.35	
	Pcacl$_2$	1	1	0.85	F = 2.81, n/s
	mg kg^{-1}	1.35	1.15	0.9	
		1.85	1.35	0.9	
	Pm	6.3	6.6	6	F = 4.14, n/s
	mg l^{-1}	7.7	7.8	5.9	
		6.3	8.1	6	
3	Pfeo	85	86	79	F = 2.62, n/s
	mg kg^{-1}	105	100	83	
		115	110	84	
	Pw	45	38	26	F = 1.81, n/s
	mg kg^{-1}	47	40	36	
		51	53	46	
	Pcacl$_2$	8.6	5.15	4.45	F = 51.6***
	mg kg^{-1}	8.75	5.95	4.65	
		9	6.8	4.9	
	Pm	28	19.5	18.3	F = 6.04*
	mg l^{-1}	22.6	19.1	18.2	
		29.6	26.3	16.4	

Site no.	**P-test**	**Sample depth**			**F-ratio**
		2 cm	**5 cm**	**10 cm**	
4	**Pfeo**	95.45	70.95	70.25	F = 12.49**
	mg kg^{-1}	100.55	77.2	76.75	
		105.15	86.8	82.8	
	Pw	41	33.2	30.6	F = 2.75, n/s
	mg kg^{-1}	50	39.2	37.4	
		68.5	44	42.4	
	Pcacl$_2$	9.75	5.25	4.6	F = 84.10***
	mg kg^{-1}	10	6	4.95	
		10.35	6.35	5.75	
	Pm	23.5	18.3	17	F = 6.19*
	mg l^{-1}	20.9	19.2	17.9	
		25	21.9	19.5	
5	**Pfeo**	31.2	22.2	19.8	F = 19.2**
	mg kg^{-1}	33	22.8	20.8	
		35.2	26.2	25.2	
	Pw	8.4	7.4	5.8	F = 4.91*
	mg kg^{-1}	10.2	8.2	6.8	
		11.8	9.2	8	
	Pcacl$_2$	2.45	1.3	1.3	F = 0.72, n/s
	mg kg^{-1}	2.8	1.45	1.85	
		3.25	4.65	2.05	
	Pm	7.7	5.6	3.5	F = 19.79**
	mg l^{-1}	6.8	5.1	3.9	
		6.4	4.3	4.4	
6	**Pfeo**	33	36	35.2	F = 0.33, n/s
	mg kg^{-1}	53.2	43.6	38.4	
		56.4	52.4	49.6	
	Pw	14.4	11.8	12.6	F = 0.31. n/s
	mg kg^{-1}	16	12.8	15.2	
		19.4	18.8	19.8	
	Pcacl$_2$	2.55	2.2	1.95	F = 2.92, n/s
	mg kg^{-1}	2.85	2.4	2.35	
		3.45	2.85	2.45	
	Pm	10.7	10.2	7.6	F = 8.19*
	mg l^{-1}	9.9	8.8	8.1	
		10.4	7.7	7.6	
7	**Pfeo**	31.2	30.95	27.05	F = 0.52, n/s
	mg kg^{-1}	34.25	36.85	31.85	
		45.95	43.3	38.15	
	Pw	17.6	14.2	12.2	F = 2.52, n/s
	mg kg–^{1}	20.6	15	14.2	
		22.6	23	16	
	Pcacl$_2$	2.9	1.9	1.1	F = 31.25***
	mg kg^{-1}	3.35	2.25	1.2	
		3.7	2.65	1.35	
	Pm	8.9	7.7	6.1	F = 3.91, n/s
	mg l^{-1}	8.7	8.5	5.7	
		8.8	5.9	7.8	

Appendix B

Percentage organic matter (%OM) and Mehlich-3 extractable Al (M3-Al) measured from composite samples taken to 2, 5 and 10 cm from each site.

Site no.		Sample depth		
		2 cm	**5 cm**	**10 cm**
1	%OM	8.8	8.2	8.1
	M3-Al (mg/kg)	673	754	748
2	%OM	11.5	8.8	7
	M3-Al (mg/kg)	641	695	782
3	%OM	12	10.3	8.4
	M3-Al (mg/kg)	561	617	661
4	%OM	10.6	9.8	8.2
	M3-Al (mg/kg)	660	656	677
5	%OM	7.5	7.6	5.9
	M3-Al (mg/kg)	656	643	654
6	%OM	7.3	6.8	6.3
	M3-Al (mg/kg)	787	762	807
7	%OM	7.7	7.5	5.9
	M3-Al (mg/kg)	690	749	761