Environmental RTDI Programme 2000–2006

EUTROPHICATION FROM AGRICULTURAL SOURCES – Phosphorus Chemistry of Mineral and Peat Soils in Ireland

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Final Report

Prepared for the Environmental Protection Agency

by

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1 Introduction

Phosphorus (P) loss to Irish rivers is of great concern and agriculturally derived P is estimated to account for almost half of Irish river pollution (McGarrigle and Clenaghan, 2004). Soil P that accumulates beyond crop requirements is a major diffuse source of agricultural P and high soil test P (STP) levels have been linked to losses in overland flow from grasslands in Ireland (Kurz *et al.*, 2005) and elsewhere (Heckrath *et al.*, 1995; Pote *et al.*, 1996). Soil P analysis is therefore used as an indicator of potential P losses from grassland soils (Lemunyon and Gilbert, 1993) and this has led to advancements in soil P analysis that focus on environmentally orientated tests designed to simulate losses to water, as opposed to P availability to plants. The objective of this study was to examine the impact of soil chemical properties on P sorption and desorption, so that a risk assessment of P loss from soil types could be developed using identifiable soil chemical characteristics.

The importance of relating soil P chemistry to general soil characteristics and STP in order to predict the risk of P loss to freshwater systems has been demonstrated in recent Irish studies (Daly *et al.*, 2002; Kurz *et al.*, 2005; Styles *et al.*, 2005). These studies used Morgan's P – the standard agronomic P test in the Republic of Ireland – as an indicator of soil P solubility and potential losses to water.

Olsen P is another STP method widely used in Europe, Australia and New Zealand, and differs from most other, acidic, P tests in that it uses an alkaline extractant ($NaHCO_3$ at pH 8.5). It is thought to be a better indicator of P availability in calcareous soils (e.g. Curtin and Syers, 2001) than acidic extractants, which, according to test characteristics, have been found to either overestimate available P through rigorous Ca-P dissolution, or underestimate available P through neutralisation in calcareous soils (e.g. Rhue and Hensel, 1983; Zbiral, 2000). Olsen P was therefore used as an additional indicator of P availability in this study, alongside Morgan's P, in order to determine whether it was a better indicator of P loss risk for calcareous soils.

Desorption methods, such as the iron-oxide impregnated paper strip test, simulate long-term desorption using a sink for P (Menon *et al.*, 1988; Chardon *et al.*, 1996) and have been used to measure bioavailable P in overland flow water (Sharpley, 1993). The iron-oxide strip test for P (FeO-P) provides a rigorous quantification of short-term desorbable P (Van der Zee *et al.*, 1987), and, in contrast to other soil P extractions, it has been found to be equally effective for calcareous and non-calcareous soils (Guo *et al.*, 1996; Menon *et al.*, 1997). It was initially thought to primarily represent bioavailable, dissolved inorganic P (Van der Zee *et al.*, 1987; Menon *et al.*, 1988). However, Robinson and Sharpley (1994) found that, whilst it was effective at extracting almost all dissolved inorganic P from (soil) solutions, much of the dissolved organic P fraction was extracted too. Some of the most abundant soil organic species, such as inositol hexakisphosphate, are strongly sorbed onto Fe oxides. Thus the FeO-P test, provides a good indication of desorbable, though not necessarily inorganic, P. Sibbesen and Sharpley (1997) recorded strong linear relationships between FeO-P and bioavailable P in surface runoff. The water-soluble P test (WSP) was first reported as a simple, effective agronomic P test by Van der Paauw (1971), but has since been adopted as a convenient indicator of immediately soluble P content in soils. A number of studies have proved it to be a useful indicator of soluble P concentrations in soil runoff water (Yli-Halla *et al.*, 1995; Sharpley *et al.*, 1981; McDowell and Sharpley, 2001; Torrent and Delgado, 2001). Both the FeO-P and the WSP tests were used as indicators of P solubility in this study.

The degree of P saturation (DPS) has been used extensively as a saturation index that combines desorbable P and sorption capacity, and is used to define thresholds of soil P as an environmental indicator (Beauchemin and Simard, 1999). Aspects of P sorption often included in the saturation index vary from the sum of extractable aluminium (Al) and iron (Fe), to a measure of P sorption capacity from isotherm experiments, thereby incorporating some feature of soil type combined with a measurement of soil P. The process of soil P sorption is commonly described by the sorption isotherm,0 initially to provide a better understanding of the behaviour of labile P and its uptake by plants (Barrow, 1967; Bache and Williams 1971) but more recently, in the context of describing the capacity of a soil to retain P against losses to water (Lookman *et al*., 1996; Borling *et al*., 2001). The advantage of describing P sorption in soils, either for agronomic or environmental purposes, is that it includes some aspect of soil type. Phosphorus sorption capacity has been related to amounts of extractable Al and Fe in soils and this has been used to model P sorption in soils with regard to different soil type characteristics (Freese *et al*., 1992; Simard *et al*., 1994; Maguire *et al*., 2001).

In this present study, the principal soil types (mineral and peat) from six mini-catchments were collected and measured for their sorption and desorption properties. An objective of this study was to describe the phosphorus chemistry of soil types, and link soil chemical properties associated with sorption and desorption processes to potential risk of P loss.

Soil sampling in this study was carried out over two different time periods. The first soil sampling (over six mini-catchments) took place in 2001. Phosphorus sorption in soil types was measured using the Langmuir sorption isotherm parameters of sorption capacity, binding energy and buffer capacity. Desorption was described using the iron-oxide paper strip test (FeO-P) and P saturation was described using an index of Mehlich-3 P and maximum sorption capacity from the Langmuir isotherms. Soil P level was described using the standard agronomic Morgan's P test.

When the analytical results from these samples were examined some of the results relating to P desorption in calcareous soils were inconclusive. This prompted a second sampling programme in 2004, to clarify some of the original findings relating to calcareous and non-calcareous mineral soils. Four of the original six mini-catchments were revisited and a range of mineral soils was collected. The same analytical procedures were applied to these samples with the inclusion of additional tests including Olsen-P, single point sorption index (PSI), total neutralising value (TNV), and water-soluble P (WSP). Soil P sorption and desorption was also carried out on field moist and dried samples to compare P solubility under natural and artificially dried conditions.

These data were used to identify soil factors controlling sorption and desorption in Irish grassland soils and assign some level of environmental risk to soils relative to each other. These results were applied to GIS data sets on soil classifications for use in a risk assessment model for P loss in Irish catchments (Daly and Mills, 2005).

2 Materials and Methods

2.1 Soil Sampling

The principal soil types (as described by great soil group or soil association) in six mini-catchments at various locations around Ireland were identified from detailed soil maps of catchments. For catchments where no detailed soil information was available, The General Soil Map of Ireland (Gardiner and Radford, 1980) was used. Soil samples were collected so that a range of STP levels, using Morgan's P, were represented in each soil group or association. Samples were taken on a field-by-field basis to 100 mm using a standard bucket sampler with approximately 30–40 cores bulked to provide a composite sample from each field.

Soil sampling was carried out from November 2000 to January 2001, prior to the spreading of fertilisers and manures. Seventy samples were collected across six mini-catchments and returned to Johnstown Castle Laboratories, oven-dried (40°C), ground and sieved (2-mm mesh) and stored in boxes at room temperature prior to analysis. A list of the catchments and their general characteristics is provided in Table 2.1.

Soil samples taken from the Dripsey, Oona, Clarianna and Grange–Rahara catchments in November 2004 and early January 2005 were divided into two subsample sets. One set was placed in plastic bags and stored at 4°C prior to analysis within 1 week. The other set of subsamples was dried in an oven at 40°C for 3 days and stored in plastic bags at room temperature prior to analysis.

2.2 Laboratory Analysis

Soil samples were analysed for Morgan's P at Johnstown Castle Laboratories, Wexford. Agronomic P, as determined by Morgan's P, was measured on 6.5 ml of soil using a buffered acetate-acetic acid reagent in a 1:5 (v/v) soil to solution ratio extracting for 30 min (Peech and English, 1944; Byrne, 1979). Mehlich-3 extraction was carried out at the Department of Plant and Soil Science at the University of Delaware using the modified Mehlich test (Mehlich, 1984) to extract P, Al, Fe, calcium (Ca), copper (Cu), magnesium (Mg), manganese (Mn), potassium (K) and zinc (Zn) at a 1:10 soil solution ratio using Mehlich-3 reagent (0.2 M CH_3COOH + 0.25 M NH_4NO_3 + 0.015 M NH_4F + 0.13 M HNO_3 + 0.001 M EDTA). Soil pH was determined on a 2:1 soil–water ratio paste and percentage organic matter (%OM) estimated as the loss-on-ignition of 5-g samples.

Olsen P was measured on a 2.0-g soil sample which was shaken with 40 ml 0.5 M $NaHCO_3$, buffered at pH 8.5, for 30 min, and MRP measured in the filtrate (Olsen *et al.*, 1954).

The iron-oxide paper strip P test was used as a 'P sink' method for estimates of labile inorganic P in soils according to the method of Menon *et al.* (1988). One iron-oxide impregnated paper strip (100 × 20 mm) was added to each sample of soil (1 g) suspended in 40 ml of 0.01 M $CaCl_2$ solution and shaken for 16 h on an end-over-end shaker. The paper strips were then eluted with 0.1 M H_2SO_4 for 1 h and the P concentration in the acidic solution determined colorimetrically.

Table 2.1. General catchment details and their principal soil types.

Catchment	Size (km^2)	Location	Parent material	Principal soil types	Soil survey source
Clarianna	28	Tipperary	Gravelly limestone till	Grey brown podzolic, peat, brown earth	UCD
Clonmore		Tipperary	Limestone till	Grey brown podzols, peat	Teagasc
Dripsey	14	Cork	Old red sandstone	Brown podzol	Teagasc
Grange–Rahara	12	Roscommon	Calcareous glacial till	Grey brown podzolic, peat	UCD
Oona	88	Tyrone	Carboniferous sandstone & limestone	Gley	University of Ulster
Yellow	20	Meath	Shales and sandstones	Acid brown earth, peat	Teagasc

Water-soluble P was measured on 1.0 g dry-weight equivalent soil, shaken with 40 ml DDW (39 ml for moist samples) for 1 h, and MRP measured in the filtrate. An additional set of water-soluble P analyses were performed after pre-moistening 1.0 g dried soil for 24 h with 2.5 ml deionised water, prior to extraction, after the addition of a further 37.5 ml of deionised water. Phosphorus concentration in filtered extracts for FeO-P and WSP tests was determined using the modified ascorbic acid method for soils by John (1970).

Total neutralising value (TNV) was measured on 2.0 g dried soil in 20 ml 0.5 M HCl over 2 h. A few drops of phenolphthalein indicator were added and the solution was titrated with 0.5 M NaOH until the whole solution remained slightly pink for more than 5 s. The volume of NaOH needed to reach this end point was calibrated against 20 ml 0.5 M HCl, and 20 ml HCl after reaction with 1.0 g pure powdered $CaCO_3$, and used to calculate weight-percentage carbonate content (Allen, 1989). Soil pH was measured using a 1:2 soil–solution ratio in deionised water.

Organic matter (OM) content was measured by loss on ignition. Moist soil (20 g) was placed in weighed crucibles, dried for 24 h at 105°C, and weight loss over this period taken as soil moisture content. For OM content, approximately 1.0 g of soil dried at 40°C was placed in a weighed crucible. Weight was again recorded, after leaving in an oven at 105°C overnight, to calculate moisture content in the soil dried at 40°C. Then, the samples were ashed for 3 h at 500°C. Percentage weight OM content was calculated from weight loss between oven-dried and ashed samples. The bulk density (BD) of soils was estimated from %OM by the method of Jeffrey (1970).

Potential P sorption to soils was estimated using the Langmuir model (Paulter and Sims, 2000) using a modification of the standardised batch technique by Nair *et al.* (1984). Six solutions of P concentration 0, 5, 10, 15, 20 and 25 mg/l P were added to 2-g soil samples in 50-ml centrifuge tubes in duplicate. The suspensions were shaken at room temperature for 24 h, centrifuged and filtered, and the concentration of P in solution measured colorimetrically (John, 1970). Phosphorus sorbed to soil was calculated as the difference between initial concentration and P concentration measured at equilibrium. Phosphorus sorption isotherms were plotted for each soil using the Langmuir model and were used to derive sorption maximum (Xm, mg/kg), binding energy (b, l/mg) and maximum buffer capacity (MBC, l/kg) as the product of Xm and b. The Xm term referred to the maximum amount of P that could be sorbed by the soil and the b term referred to the intensity/stability of P sorption. Maximum buffer capacity in soils was defined as a measure of the ability of a soil to resist a change in the concentration of P in solution. A high MBC indicated a strong resistance to change in solution concentration and *vice versa* (Bolland and Allen, 2003; Bertrand *et al.*, 2003). All mineral calcareous and non-calcareous soils fitted the Langmuir model ($R^2 > 0.95$) whilst peat soils (or soils with OM>20%) did not conform to the Langmuir model. The DPS was calculated using Mehlich-3 extractable P and Xm, expressed as a percentage (Sharpley, 1995).

Sorption isotherms were derived for all soils collected in 2001 and for 16 soils collected in 2004 representative of low and high soil pH.

A single-point P sorption index was derived for calcareous and non-calcareous mineral soils taken in 2004 using 0.5 g dry-weight equivalent soil shaken with 50 ml 0.02 M KCl solution containing 40 mg/l P (resulting in a P loading of 4000 mg P per kg soil). An initial PSI was attempted using 400 mg/l P solution at a soil–solution ratio of 1:10, but the dilution factor required for MRP measurement was too high, and final relative solution P concentration differential too small.

Two methods were used to calculate phosphorus sorption capacity (PSC) using the PSI measurement. Firstly, M3-P was added to the PSI for each soil to give PSC1 (mg/l soil). Secondly, the sum of molar M3 extractable Al and Fe concentrations was multiplied by an activity factor of 0.5 (as defined by Freese *et al.*, 1992, for oxalate-extractable Al and Fe) to give PSC2 (mmol/l soil).

3 Results and Discussion

3.1 General Soil Characteristics

Soil samples taken across the six catchments in 2001, comprising of mineral and peat soils, displayed a range of general soil properties. Soil pH ranged from 4.7 to 7.3 (mean 5.8) and %OM ranged from 5.3 to 43 (mean 11.5%). Summary statistics of P and non-P data are presented in Tables 3.1 and 3.2. The peat soils from the Clonmore, Clarianna and Grange–Rahara catchments, had OM levels above 20%. The pH of non-calcareous mineral soils, in general, ranged from 4.7 to 6.0. The average Morgan's P value across all soils was 7.2 mg/l and ranged from 1.5 to 17.5 mg/l.

Soil chemical parameters, such as extractable Al, Fe, Ca, Mg and Mn, were all strongly correlated with soil pH and these elements were measured in both non-calcareous and calcareous mineral soils sampled in this study. Within the mineral soils, extractable Al (R^2 = 0.68***) and Fe (R^2 = 0.19***) were negatively correlated with soil pH with values of both metals significantly higher in non-calcareous soils compared to calcareous soils ($p < 0.001$). Conversely, extractable Ca (R^2 = 0.61***), Mg (R^2 = 0.14**) and Mn (R^2 = 0.14**) were positively correlated with pH and values of these metals were significantly higher in calcareous soils compared to non-calcareous soils. The relationships between Al, Fe, Ca and pH across mineral soils are presented in Figs 3.1–3.3. Extractable Ca ranged from 284.3 to 32,104 mg/kg (mean 3598.8 mg/kg) with the highest measured in calcareous soils of the Clarianna and Clonmore catchments. Conversely, the highest Al levels were measured in the non-calcareous soils of the Oona catchment and values ranged from 69 to 1330 mg/kg. Extractable Fe was highest in the non-calcareous soils of the Dripsey catchment and values ranged from 75 to 618.8 mg/kg. Analytical data of soil samples taken in 2004 from four of the six mini-catchments are summarised in Tables 3.3 and 3.4.

3.2 Moist and Dried Sample Analyses

In line with other studies, overall, drying the soils was found to significantly increase soluble P (measured here in the form of WSP and FeO-P). However, the mean increases in WSP and FeO-P after drying were similar and small (3.32 mg/l, or 50%, and 3.36 mg/l, or 16%, respectively) compared with soluble P increases found by Turner and Haygarth (2001) and Styles *et al.* (2005). Drying-induced changes in WSP were significantly positively correlated with OM content ($r = 0.59$, $p < 0.0001$), but not with pH or Ca, and drying-induced changes in FeO-P were not significantly correlated with any of these soil characteristics. The positive correlation between drying-induced WSP increases and OM is consistent with drying-induced P release associated with OM oxidation and disruption during the drying and

Table 3.1. Phosphorus sorption and desorption in all soil types collected (n = 70); peat soils are not included in Langmuir sorption terms.

Statistic	Morgan's P (mg/l)	Feo-P (mg/l)	M3-P (mg/l)	Xm (mg/kg)	b (l/mg)	MBC (mg/kg)	DPS (%)
Min	1.5	14.3	2.2	263	0.35	119	4.4
Max	17.5	60.7	174.5	625	7.67	3333	48.4
Mean	7.2	30.2	55.6	421	1.85	816	17.6

Table 3.2. General soil characteristics measured across all mineral and peat soils collected in 2001 (n = 70).

Statistic	pH	OM	BD*	Al	Fe	Ca	Cu	Mg	Mn	K	Zn
		(%)	(g/ml)				(mg/kg)				
Min	4.7	5.3	0.4	69	75	284	0.9	58	20	59	2.5
Max	7.3	43	1.0	1330	619	32,104	10.8	544	217	420	21.5
Mean	5.8	11.5	0.8	809	430	3,599	3.8	154	87	171	6.0

*Estimated from %OM (Jeffrey, 1970).

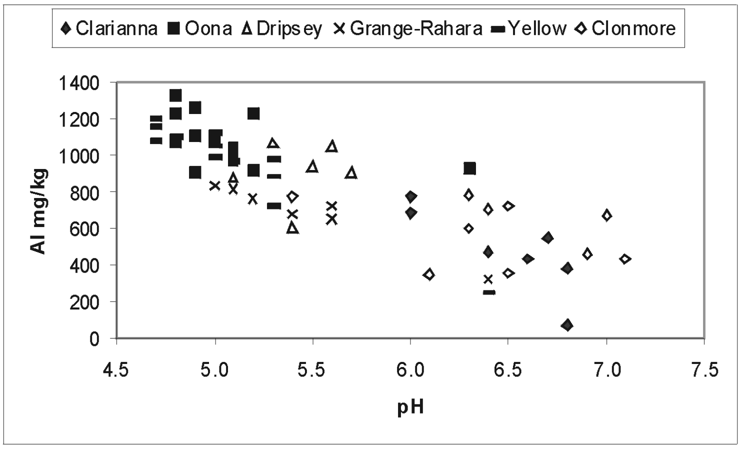

Figure 3.1. The relationship between extractable Al and pH in mineral soils ($R^2 = 0.68$***).

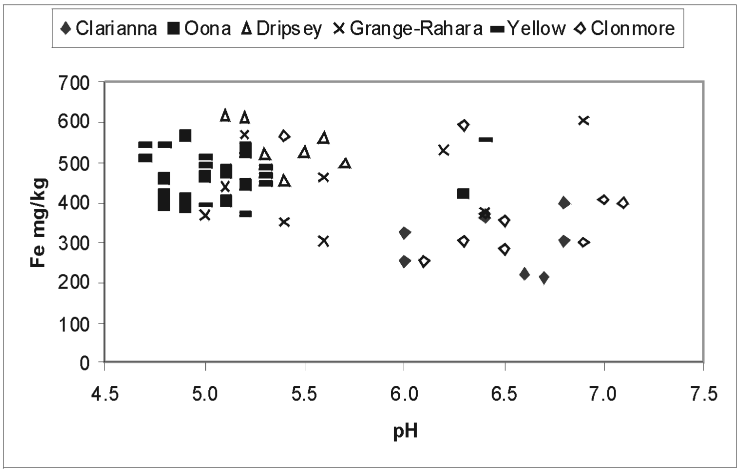

Figure 3.2. The relationship between extractable Fe and pH in mineral soils ($R^2 = 0.19$***).

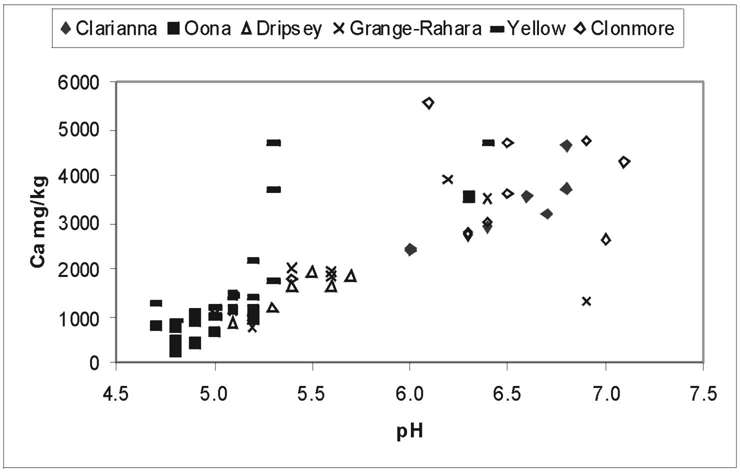

Figure 3.3. The relationship between Ca and pH in mineral soils ($R^2 = 0.61$***).

Table 3.3. Phosphorus characteristics of mineral soil types collected in 2004 (n = 62), Langmuir parameters measured on 16 samples.

Statistic	Morgan's P	M3-P	Olsen P	WSP	FeO-P	PSI	PSC1	PSC2	Xm	b	MBC
	(mg/l)						(mmol/l)		(mg/kg)	(l/mg)	(mg/kg)
Min	1.5	9	6	2.3	2.5	59	136	10	244	0.2	114
Max	32.9	196	68	21.1	56.9	479	495	28	667	8	3333
Mean	9.8	76	29	9.5	24.2	214	289	19	404	2.8	1187

Table 3.4. General soil characteristics measured across all mineral soils collected in 2004 (n = 62).

Statistic	pH	OM	TNV	Al	Fe	Ca	Cu	Mg	Mn	K	Zn
		(%)		(mg/kg)							
Min	4.9	5.7	0	401	195	389	2.8	1	9	2	2.7
Max	6.8	15.7	9.9	1301	545	4309	15.6	651	249	419	22
Mean	5.5	11.3	0.9	795	432	1802	8.3	140	87	201	7

rewetting process (Raveh and Avnimelech, 1978; Olsen and Court, 1982; Chepkwony *et al.*, 2001; Turner *et al.*, 2003). Turner *et al.* (2002) found WSP increases to be dominated by the molybdate–unreactive P fraction, which was not analysed in this study. This, and the fact that water extracts were only primary filtered through Whatman no. 2 filter paper in this study, could be responsible for the relatively small drying-induced WSP increases noted here compared with other studies.

Comparatively small drying-induced FeO-P increases appear to be caused by separate mechanisms to those responsible for WSP increases. Firstly, there should not have been an interfering effect from fine colloidal P in the FeO-P analysis. Secondly, the weak electrolyte (0.02 M KCl) solution used in the FeO-P analysis may have suppressed any osmotic shock of rehydration sufficiently to have prevented microbial cell lysis (Kieft *et al.*, 1987), thus accounting for the proportionately much smaller drying-induced percentage increase for FeO-P compared with WSP. However, the absence of correlation between drying-induced FeO-P changes and OM content indicates that the (re)exposure of (de)sorption sites through drying-induced OM-aggregate disruption is not a dominant factor. Pote *et al.* (1999a) and Styles (2004) found that drying soil samples masked much of the seasonal variation in P solubility caused by such effects. Thus, although drying soil samples may obscure genuine variations in readily soluble P amongst soils, the use of dried soil P solubility data for the purposes of this study is not redundant: dried samples may provide a useful indication of potentially soluble P that is somewhat buffered against the confounding effects of season/antecedent meteorological conditions.

3.3 Phosphorus Sorption and Desorption in Mineral and Peat Soils

Soil sampling carried out in 2001 was conducted to capture a range of STP levels, as measured by Morgan's P, across mineral and peat soils of varying organic matter and bulk densities. Phosphorus desorption data (FeO-P and M3-P) were expressed on a volume basis using BD of soils so that the units were comparable with the Morgan's P test and would consider the wide variation in BD across mineral and peat soils. There were significant differences ($p < 0.001$) in FeO-P and M3-P values between mineral and peat soils such that, over a similar range in Morgan's P levels, desorption from peat soils was significantly lower compared with mineral soils. This concurs with earlier work by Daly *et al.* (2001) and with recent work by Styles (2004), confirming that low desorption in peat soils is due in part to their limited capacity to chemically bind P and create any P reserves.

All of the mineral soils in this study conformed to the Langmuir sorption model ($R^2 > 0.95$); however, sorption isotherms could not be derived for peat soils, since they did not conform to the model using the method adopted in this study. This may have been due to the high amounts of organic matter in peat soils that may have inhibited or blocked P sorption sites and concurs with earlier work on P sorption in peat soils (Daly *et al.*, 2001).

3.4 Phosphorus Sorption in Calcareous and Non-Calcareous Mineral Soils

The Langmuir sorption isotherm parameters Xm, b and MBC were negatively correlated with soil pH in mineral soils (collected in 2001) and all of the sorption parameters decreased as soil pH increased (Figs 3.4 to 3.6). Maximum sorption capacity, Xm, was negatively correlated with pH (R^2 = 0.23***), and decreased as pH increased. Hypothesis testing between non-calcareous and calcareous soils returned significant differences about the mean ($p < 0.001$) and median ($p < 0.001$) with higher sorption capacities measured in non-calcareous soils. The binding energy, b, decreased non-linearly with pH and values were significantly higher in non-calcareous soils ($p < 0.001$). Similarly, MBC decreased with increasing soil pH (R^2 = 0.37***) and values in non-calcareous soils were significantly higher than calcareous soils ($p < 0.001$). Soil samples collected in 2004 showed similar trends and sorption measurements PSI, PSC1 and PSC2 were all significantly, inversely correlated with pH and Ca. In addition, measures of PSI and Langmuir terms Xm, b and MBC were all significantly ($p < 0.0001$) lower in calcareous soils than non-calcareous soils, with highest values measured in non-calcareous mineral soils. The PSI was found to be significantly lower in calcareous than non-calcareous soils, in both moist and dried sample analyses.

All of the Langmuir sorption parameters Xm, b and MBC were positively correlated with extractable Al across the range of mineral soils; however, these correlations were only significant in the non-calcareous soils. Maximum sorption capacity was positively correlated with extractable Fe across calcareous (R^2 = 0.36**) and non-calcareous soils (R^2 = 0.25**). In a multiple regression model (R^2 = 0.72), Xm was described by Al, Fe and %OM as positive predictors. Phosphorus binding energy (b) was described in a multiple regression model (R^2 = 0.63) using Al as a positive predictor and %OM as a negative predictor. These equations are shown in Table 3.5.

Extractable Al correlated with both Xm and b, providing strongly bound sites for sorption. Both Al and Fe are recognised soil factors that influence sorption capacity in soils (Freese *et al*., 1992; Beauchemin and Simard, 1999; Borling *et al*., 2001); however, the inclusion of %OM as a variable is not as common as using Al and Fe. The equations in Table 3.5, describing Xm and b using %OM, suggest that whilst sorption surfaces can be provided by OM, the P binding energies were negatively affected by OM, suggesting weaker P binding energies associated with OM surfaces.

Amongst non-calcareous soils collected in 2004, regression analyses between PSC1 and the major soil characteristics indicated that extractable Al was the dominant predictor of sorption capacity (R^2 = 0.64, $p < 0.0001$) and the inclusion of OM content was significant as a positive predictor (p = 0.023) and marginally increased R^2 to 0.66. This concurred with the earlier finding reported in soils taken in 2001.

For calcareous soils, only the regression equation predicting Xm using extractable Fe was improved with the inclusion of Ca (R^2 = 0.65) in a multiple regression model. However, amongst calcareous soils collected in 2004, no significant association was found between PSC1 and extractable Al, Fe, Ca, pH or OM content.

3.5 Phosphorus Desorption in Mineral Soils

The standard agronomic P test, Morgan's P, was strongly correlated with desorption tests FeO-P (R^2 = 0.63***), M3-P (R^2 = 0.66***) and DPS (R^2 = 0.69***), across the range of mineral calcareous and non-calcareous soils collected

Table 3.5. Multiple regression model for P sorption capacity and binding energy using Al, Fe, %OM and pH in non-calcareous soils.

Y	Variable	Coefficient	SE of coefficient	Probability	R^2
Xm	Al	0.31	0.05	<0.0001	0.72
	Fe	0.36	0.12	<0.0042	
	%OM	15.7	3.4	<0.0001	
B	Al	0.01	0.001	<0.0001	0.63
	%OM	–0.16	0.06	0.015	

SE, standard error.

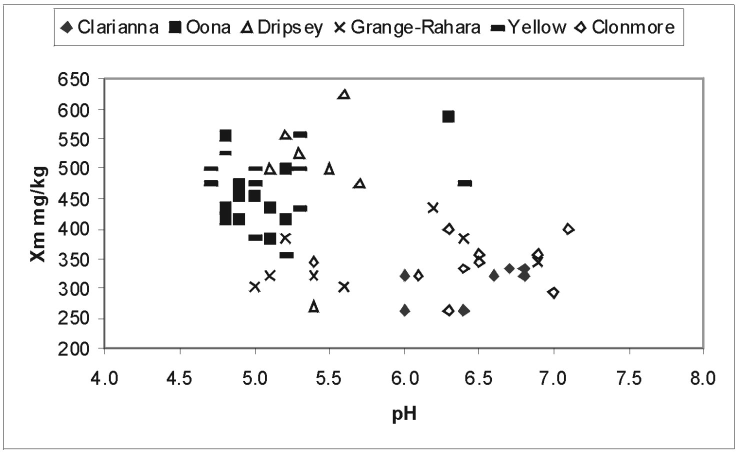

Figure 3.4. Phosphorus sorption capacity plotted against pH in non-calcareous and calcareous mineral soils.

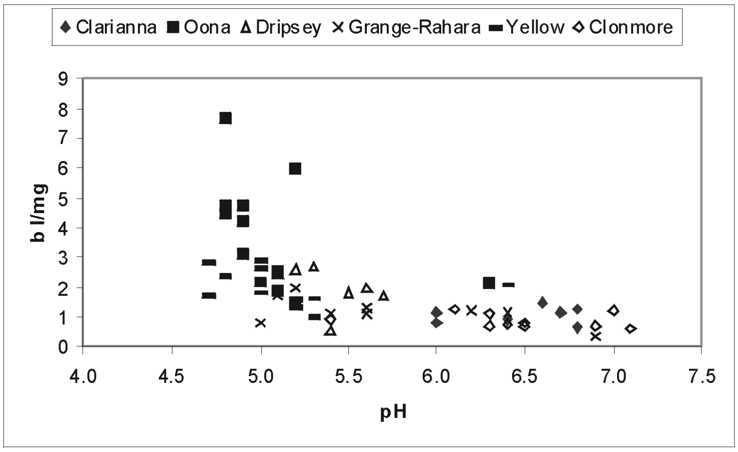

Figure 3.5. Phosphorus binding energy, b, plotted against pH in non-calcareous and calcareous mineral soils.

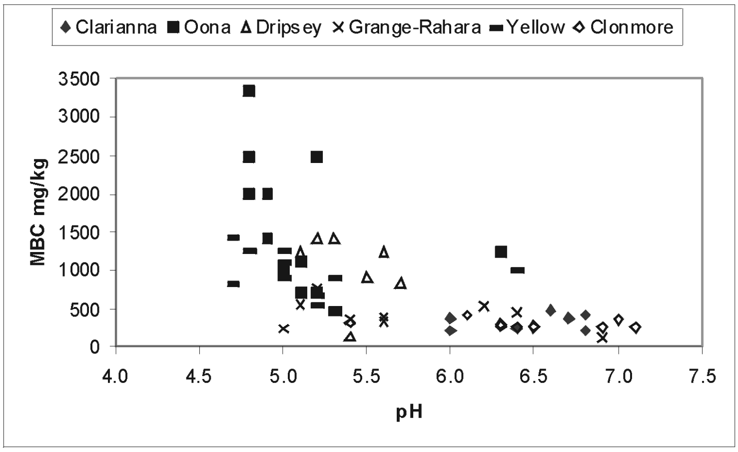

Figure 3.6. Maximum buffer capacity plotted against pH in non-calcareous and calcareous mineral soils.

in 2001, thus Morgan's P alone was a reasonably good predictor of P desorption and saturation. This finding concurs with work carried out evaluating Morgan's P as an indicator of agronomic P and potential losses in laboratory studies (Jokela *et al*., 1998; Daly *et al*., 2001; Humphreys *et al*., 2001; Styles, 2004) and plot-scale studies (Kleinman *et al*., 2000).

3.6 Effect of pH on P Sorption–Desorption Dynamics in Non-Calcareous Soils

Phosphorus desorption (FeO-P) and saturation (DPS) measured in mineral soils collected in 2001 are plotted against soil pH in Figs 3.7 and 3.8, respectively, with positive correlations with pH and FeO-P (R^2 = 0.35***) and DPS (R^2 =0.28***) in non-calcareous soils only (pH 4.7–6). These positive correlations between P desorption and pH, within the non-calcareous pH range 4.7–6, indicate that P is more soluble under neutral conditions. The inverse relationship between P sorption parameters and pH shown in Figs 3.4 to 3.6, within this pH range confirms this: P binding energies were higher under strongly acidic conditions (low pH 4.5–5) compared to neutral conditions (pH 6); thus, higher desorption values under neutral conditions are expected. From an agronomic perspective, neutral soil conditions are essential (pH 6.3) to ensure optimum P availability for crops, and soil pH in isolation is not necessarily an

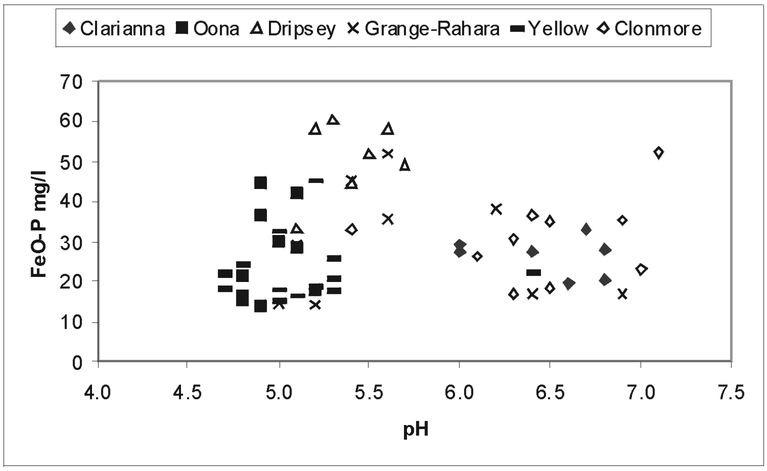

Figure 3.7. Iron-oxide strip P plotted against pH in non-calcareous and calcareous mineral soils.

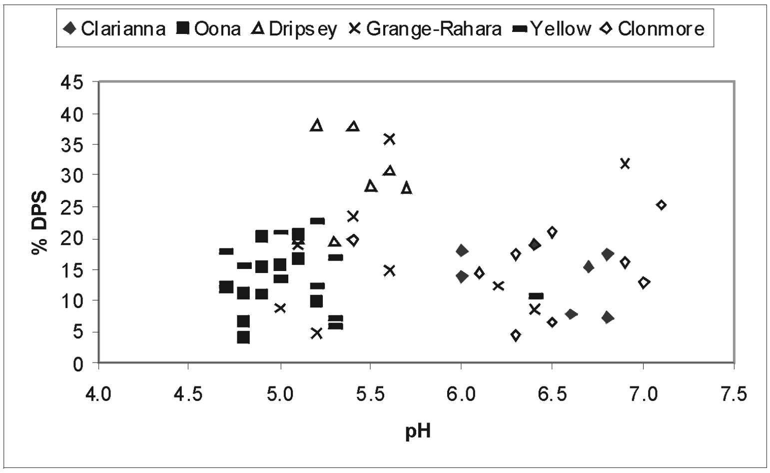

Figure 3.8. Degree of P saturation plotted against pH in non-calcareous and calcareous mineral soils.

environmental risk factor without the additional information confirming excessively high soil P level. When calcareous soils only were analysed, no significant relationship between P and pH was found which suggests that these soils may be buffered against changes in soil pH.

Soil samples taken in 2004 did not indicate any significant correlation between P desorption/solubility and pH within non-calcareous soils. This may have been due to the slightly higher pH values in lower range, from 4.9 to 6, compared to values measured in 2001 that ranged from 4.7 to 6. The low pH, acid brown earths collected from the Yellow catchment were not included in the 2004 sample data, and the absence of strongly acidic soils from these data may have affected the correlation between P desorption and pH.

However, across all of the 2004 soil data (calcareous and non-calcareous), a significant interaction between pH and Morgan's P was found using ANCOVA to predict FeO-P and WSP, which suggests that, once the dominant effect of soil P level (Morgan's P) on P desorption and solubility is accounted for, pH becomes an important effect. This finding is discussed in the following sections in the context of comparing P desorption between calcareous and non-calcareous soils.

3.7 Phosphorus Desorption in Non-Calcareous and Calcareous Soils

The decline in P sorption capacity and binding energies as soil pH increased from 4.7 to 7.3, especially the significantly lower sorption values measured in calcareous soils, prompted the question whether calcareous soils with low sorption capabilities released more soluble P compared to non-calcareous soils given their low binding energies and sorption capacities? This seemed particularly relevant, given the low stream ortho-P concentrations and losses measured from the Clarianna catchment in contrast to the Oona and Dripsey catchments.

Soil data from samples collected in 2001 were divided into non-calcareous (pH 4–6) and calcareous (pH 6.1–7) groups to test for differences in P desorption. Whilst both groups had a similar range of Morgan's P values, hypothesis testing performed on FeO-P, M3-P and DPS returned a non-significant difference in FeO-P and DPS but significant differences about the mean ($p = 0.0009$) and median ($p = 0.0031$) in M3-P values between the two soil groups with lower M3-P values measured in calcareous soils. This difference in M3-P values between the soils is discussed later in the context of M3-P extraction efficiency in calcareous soils.

Similar hypothesis testing between non-calcareous and calcareous soils was carried out on soil samples collected in 2004. These data contained a higher range of Morgan's P values (1.5–32.9 mg/l, mean 9.8 mg/l) compared with earlier data collected in 2001 (1.5–17.5 mg/l, mean 6.6 mg/l), with substantially higher Morgan's P values in calcareous compared with non-calcareous soils (13.5 compared with 8.7 mg/l, respectively) in the 2004 data. Analysis of soil samples collected in 2004 showed that, despite the lower laboratory sorption capability of calcareous soils, and their higher Morgan's P content, soluble P contents were not significantly higher in these soils than in non-calcareous soils.

3.8 The Effect of Soil Type on Morgan's P–P Desorption/Solubility Relationships

Higher Morgan's P values measured in the calcareous soils collected in 2004 may have limited the capability to statistically distinguish P solubility, regardless of initial soil P level, between the two soil groups; nevertheless, some significant differences were found. Whilst Morgan's P, has been found to be a useful indicator of soluble P loss risk (Pote *et al.*, 1999b; Daly *et al.*, 2002; Kurz *et al.*, 2005; Styles *et al.*, 2005), to establish any differential in P solubility (P loss risk) between soil groups, with meaningful management implications, P desorption and solubility should be studied with reference to Morgan's P. One method of doing this is to use P desorption/Morgan's P ratios (Daly *et al.*, 2002; Styles *et al.*, 2005). When ratios were calculated for calcareous and non-calcareous soils, a significant difference ($p < 0.05$ for ANOVA on normalised data) was found in the FeO-P/Morgan's P ratio between these soil groups, with lower values found in calcareous soils. The application of this method here found that the mean FeO/Morgan's P was significantly different between soil groups, and visual inspection of the FeO-P – Morgan's P relationship (Fig. 3.9) indicated that it took on a different (non-linear) form in calcareous soils from the linear form displayed in non-calcareous soils.

As mentioned earlier, when an interaction term between pH and (log-transformed) Morgan's P was included in ANCOVA, run separately with each of the soluble P measures as dependent variables, it was found to be significant for (square-root transformed) WSP ($F_{1,56}$ = 5.308, p = 0.025) and FeO-P ($F_{1,56}$ = 13.279, p = 0.0006). Results were similar when an interaction term between Morgan's P and Ca was included. This confirmed what Fig. 3.9 indicated that the Morgan's P–FeO-P relationship is different at different soil pH values. The curvilinear relationship between FeO-P and Morgan's P in calcareous soils highlights a limitation of using mean soluble P/Morgan's P ratios to indicate differences in P solubility characteristics between calcareous and non-calcareous soils, at excessively high P level: these ratios assume a linear P solubility/Morgan's P relationship. Furthermore, the data here suggest similar desorption at lower Morgan's P, but relatively lower desorption at higher Morgan's P, for calcareous compared with non-calcareous soils. In light of this finding, the relationship between FeO-P and Morgan's P in the earlier 2001 data was re-examined by dividing soils into calcareous and non-calcareous groups. Visual inspection of the P desorption–Morgan's P relationship (Fig. 3.10) for soils collected in 2001, within a Morgan's P range of 1.5–17.5 mg/l, confirms what the subsequent data in 2004 reported: that differences in desorption are similar at lower Morgan's P values.

The significant interactions between pH and Morgan's P in ANCOVA to predict WSP and FeO-P suggest that, once the dominant effect of STP (Morgan's P) on soil P solubility is accounted for, pH becomes an important

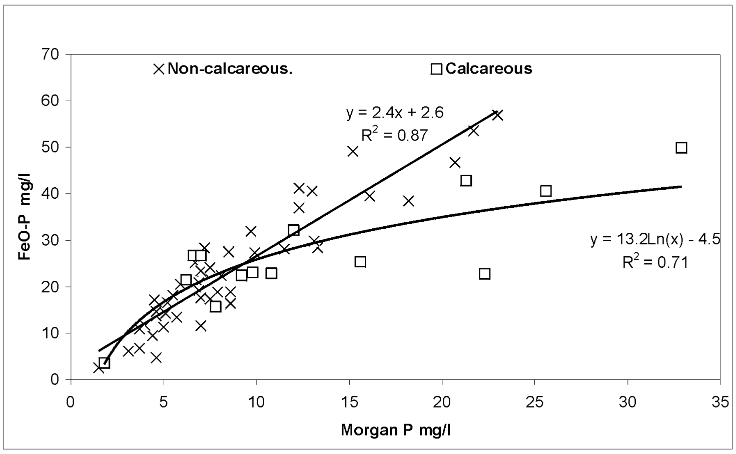

Figure 3.9. The relationship between Morgan's P and FeO-P in non-calcareous and calcareous soils from mineral soil data collected in 2004.

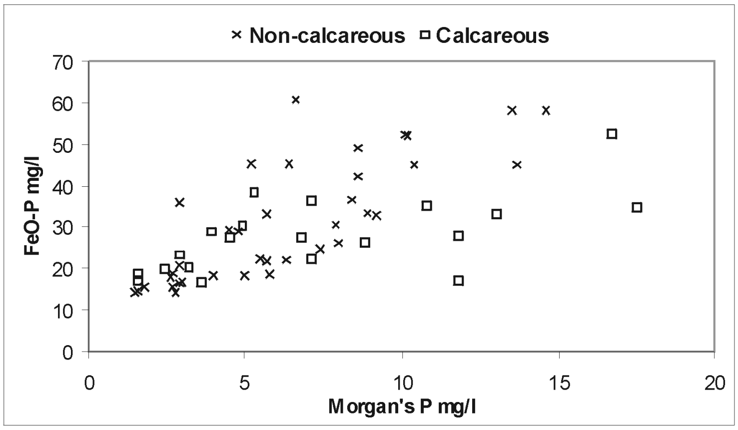

Figure 3.10. The relationship between Morgan's P and FeO-P at lower Morgan's P levels in mineral soils collected in 2001.

effector of P solubility from soils. To focus in on pH effects, soils were divided into calcareous and non-calcareous soil groups, according to their pH, and an interaction term 'soil group' was used in the following ANCOVA analyses. An interaction term between (log-transformed) Morgan's P and soil group (calcareous or non-calcareous) proved to be significant in ANCOVA analyses with (square-root transformed) Olsen P and FeO-P as dependent variables ($F_{1,57}$ = 4.973 and 10.333, $p < 0.0297$ and 0.0022, respectively), confirming that these relationships differed between calcareous and non-calcareous soils. The relationship between Morgan's P and Olsen P is discussed later in this section.

The FeO-P test is a more rigorous test for desorbable P than the rapidly soluble WSP test. Thus, this study contributes further evidence of contrasting P desorption behaviour, specifically STP–P desorption relationships, between contrasting soil types.

The consequent implications of these results for both management and environmental recommendations for these soils would be minimal, given that the real difference in the FeO-P–Morgan's P relationship occurred at very high Morgan's P concentrations above the Teagasc-recommended values. However, the FeO-P–Morgan's P relationship may provide a possible 'soil chemistry' explanation for low soluble P losses from the Clarianna catchment, if, as has been suggested, most soil P losses originate from relatively small critical source areas, where high soil P levels and high hydrological connectivity coincide (Gburek *et al*., 2000). Data from this study would suggest that high soil P areas from non-calcareous catchments desorb more P than high soil P areas from calcareous catchments. Combined with the lower hydrological connectivity observed in the Clarianna's predominantly freely draining soils, this would suggest smaller and less intense critical source areas in this catchment compared with non-calcareous catchments.

3.9 Phosphorus Sorption/Desorption in Calcareous Soils

Lower P desorption per unit Morgan's P at high soil P levels in calcareous soils would indicate that at least part of the reason for relatively low P transfers from soil to water in calcareous catchments – such as the Clarianna – could be due to soil P chemistry differences. However, the significantly lower binding strengths exhibited by calcareous soils are difficult to reconcile with lower P solubility per unit Morgan's P. One reason hypothesised here is an overestimation of non-calcareous binding energies and buffer capacities due to high P concentrations added to soils to derive the P sorption isotherms. The high P concentrations used in sorption experiments may not be representative of natural sorption equilibria, and may overestimate the natural P binding capability of non-calcareous soils through overemphasis of high energy (Fe and Al oxide) sorption sites that may not normally be involved in reversible P sorption. In the desorption experiments, and under natural conditions, high energy sorption sites may be less involved in P sorption, and weak Ca-P precipitation may become relatively more important in binding and buffering against P desorption.

On the other hand, high P sorption capacities in non-calcareous soils coupled with large amounts of Al and Fe do indicate a greater potential for P storage and build-up of P reserves than calcareous soils with lower sorption capacities. Where large P reserves exist, this also presents a greater likelihood of P release to solution when the opportunity arises, i.e. during overland flow and under conditions of high soil P saturation. However, the high P binding energies are more difficult to reconcile with high desorption (at high soil P) since this Langmuir parameter is meant to represent the intensity and stability of sorbed P. Nonetheless, if the capacity for sorption and build-up is great then the potential for soluble P release may also be great, under high soil P and overland flow conditions.

3.10 Olsen P and Mehlich-3 P Extraction in Calcareous Soils

As mentioned earlier, the interaction term between (log-transformed) Morgan's P and soil group (calcareous or non-calcareous) proved to be significant in ANCOVA analyses with (square-root transformed) Olsen P and FeO-P as dependent variables ($F_{1,57}$ = 4.973 and 10.333, $p < 0.0297$ and 0.0022, respectively), confirming that these relationships differed between calcareous and non-calcareous soils.

Figure 3.11 displays the differing relationship between Olsen P and Morgan's P in calcareous compared with non-calcareous soils. At low soil P, the Olsen reagent extracted significantly more P than the Morgan reagent, with a positive y intercept in Fig. 3.11, representing the capability of the Olsen reagent to extract moderately labile organic P fractions from soils very low in inorganic P, and, therefore, with negligible Morgan's P content. In these soils, pH had a more significant effect on the Morgan's P–Olsen P relationship than that documented by Foy *et al.* (1997) for cross-border Irish soils. Curtin and Syers (2001) and Sorn-Srivichai *et al.* (1984) also noted that Olsen P concentrations decreased as soil pH was increased by lime application. The latter authors suggest that P precipitates with Ca in high Ca content soils during alkaline Olsen extraction, although Naidu *et al.* (1987) attributed increased Olsen P extraction efficiency above pH 6.0 (after extraction minima between pH 5.5 and 6.0) to the slow release of Ca-P.

The Mehlich-3 reagent has also been found to be less efficient at P extraction from calcareous soils. In both the 2001 and 2004 soil data, significant differences about the mean (p = 0.0009) and median (p = 0.0031) in M3-P values between the two soil groups were found with lower M3-P values measured in calcareous soils. Lower extractable M3-P levels at high soil pH and problems using M3-P on calcareous soil have been reported in the literature (Mallarino, 1999) due to high amounts of Ca. Zbiral (2000) found that soils with a pH above 7.1 and Ca values above 4,000 mg/kg increased the pH of the M3-P extractant and the P extracted needed to be corrected or adjusted to account for this. In this present study, Ca values in Irish calcareous soils ranged from 1325 to 5542 mg/kg, exceeding the critical value set by Zbiral (2000) and this may have caused the significantly lower M3-P values in the calcareous soils. However, an earlier study on the efficiency of M3-P concluded that it was a more effective extractant than Olsen's reagent on calcareous soils (Buondonno *et al.*, 1992) and literature studies appear to offer diverging opinions on the use of this extractant in alkaline soils.

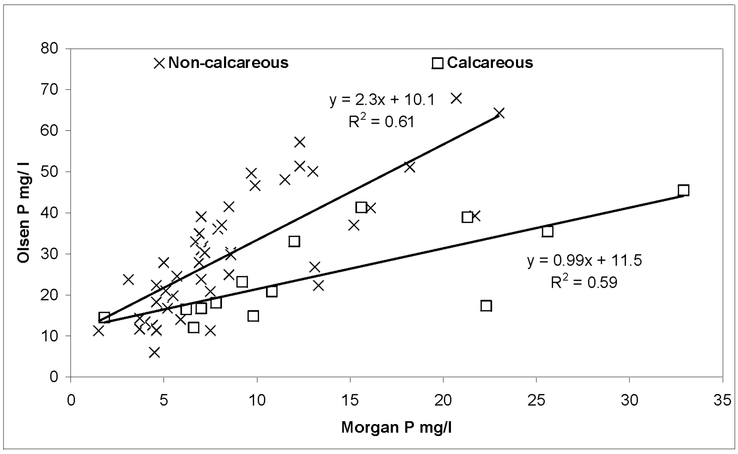

Figure 3.11. The relationship between Morgan's P and Olsen P in non-calcareous and calcareous mineral soils collected in 2004.

4 Conclusions and Recommendations

4.1 Conclusions

4.1.1 Phosphorus chemistry of soils from the Clarianna, Dripsey and Oona catchments

One of the objectives of this project was to provide some information on the soil P chemistries of the Oona, Clarianna and Dripsey catchments. These catchments were the focus of a recent catchment monitoring study (Kiely *et al*., 2005). The chemistry of the Oona and Dripsey soils are characterised here as non-calcareous soils that followed a pattern of sorption and desorption controlled by soil factors such as pH, Al, Fe and %OM. In terms of desorption to solution, high STP tended towards higher P desorption and desorption was also influenced by pH. In the Oona samples, the high levels of Al, perhaps insoluble under acidic conditions, ensured high P binding energies and less P desorption relative to the neutral soils of the Dripsey catchment. The Dripsey catchment soils were characterised as neutral soils with high DPS and desorption values that responded to an increase in soil pH. Amounts of Al in Dripsey soils were relatively small compared to the Oona catchment, with Fe being the dominant element in these soils. The soils of the Clarianna catchment fell into the calcareous category of soils, determined in this study by soil pH > 6, and, despite their significantly lower sorption capabilities, they displayed relatively lower desorption per unit Morgan's P at high P levels compared to soils from the other catchments. The lack of overland and interflow in the Clarianna, coupled with the relatively lower soil P desorption at high STP values, could explain the low in-stream P concentrations in this catchment.

4.1.2 Effects of soil type on P chemistry in Irish soils

In mineral soils, high STP values led to greater amounts of P desorption and saturation.

Peat soils and high organic matter soils (%OM > 20) did not chemically adsorb P in the same way that mineral soils do. Surface applications of manure and fertiliser P on peat soils may be lost to water if P is not sorbed into the soil. In grassland peat soils, a risk of P loss will occur if fertiliser and manure P are applied and not utilised immediately by the crop. Unlike mineral soils, peat soils do not have a capacity to fix or store applied P as unavailable occluded fractions that can be made available when a demand for P occurs during the growing season. The concept of P 'build-up' cannot be applied to peat soils in the agronomic sense and advice needs to be tailored to account for this. These soils are vulnerable to P loss through a lack of sorption capacity and binding energy rather than high rates of desorption to solution.

Phosphorus desorption was affected by soil pH in non-calcareous mineral soils, such that soils that were neutral in status desorbed more P to solution than soils that were strongly acidic. Phosphorus binding energy was affected by Al and %OM in non-calcareous soils, such that soils with high amounts of Al (and low pH) had high P binding energies, whilst mineral soils with high %OM held P less strongly. The sorption-desorption dynamics in non-calcareous mineral soils were affected by pH and/or the presence and solubility of Al under strongly acidic and neutral conditions.

Across non-calcareous and calcareous soils, pH affected the relationship between Morgan's P and P desorption. Phosphorus desorption in calcareous and non-calcareous soils, per unit Morgan's P, was similar at low Morgan's P levels (within agronomic limits) but desorption from calcareous soils was lower when Morgan's P levels increased beyond the recommended agronomic values.

4.2 Recommendations

Soil P levels should not exceed crop requirements.

Phosphorus applications on peat soils should not be managed in the same way as mineral soils; there is a need for more tailored guidelines for intensively managed grassland peat soil.

Differences in soil types should be considered in all catchment and river basin district studies when P losses to surface waters are under investigation. Excessively high soil P levels on all soils should be avoided due to their high P desorption potential, especially those soils that displayed higher desorption per unit Morgan's P at high P levels, i.e. non-calcareous soils. Excessively high soil P levels on mineral soils with high OM should be avoided, particularly those soils approaching peat soil types such as peat gleys and peaty podzols.

This project recommends that a detailed soil survey is completed on a national level, so that soil parameters such as pH and %OM, included in the survey bulletins, can be used, alongside STP level, as a guide towards high desorption soils and peat soils where heavy applications of P should be avoided. Identifying soils at risk of P desorption might be used towards developing P management strategies that are more soil type specific.

A national soil P testing survey is also recommended so that excessively high soil P areas on high desorbing soils can be identified. For the identification of critical source areas within catchments for P risk assessment, STP levels are essential, not only as an indicator of risk, *per se*, but coupled with information on soil type, these data could pinpoint high desorbing soils at high STP levels and highlight the most intense P desorbing areas within a catchment. A national soil P testing survey should consider testing on a field-by-field basis so that the information could be compatible with field-by-field risk assessment schemes (Magette *et al.*, 2005) that may be required under the Water Framework Directive (Council of the European Communities, 2000) and provide some detailed agronomic information to farmers.

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