An investigation into the overland flow and yield factors of an organic phosphate fertilizer on grassland under an intensive and a sustainable nitrogen fertilizer programme.

by

Michael Walsh B. Agr. Sc.

Supervised by

Dr. Eddy Fitzgerald

Submitted in fulfilment of the requirements of M. Sc.

With thanks to my family, Bernadette, Stephen and David for their continued support, encouragement and friendship.

Declaration

No element of this work described in this thesis, except where otherwise acknowledged, has been previously submitted for a degree at this or any other institution. The work in this thesis has been performed exclusively by the author.

Signed:

Date   : ------------------------------

ACKNOWLEDGEMENTS

CONTENTS

LIST OF FIGURES

Chapter 2

Chapter 3

List of Tables

Chapter 1

Chapter 2

Chapter 3

ABSTRACT

A comparison was made of the overland flow of P between an organic granule fertilizer Duofos (Guano; 22% P_2O_5) and Triple Superphosphate (38% P_2O_5) on a seven year-old pasture (*Lolium perenne L.*) with a gentle slope (1:20) using two 'drip-type' rainfall simulators during July 2004 and March 2005. Despite very dry weather conditions during the first half of July 2004 and a major soil moisture deficit, there was significantly lower overland flow in the case of Duofos compared with TSP. An additional very important advantage of Duofos was demonstrated following a 48 hour period of rainfall. Significantly higher concentrations of DRP, acid-hydrolyzable P and total P were recorded in the case of TSP after this rain. Duofos had a much higher organic matter content (86g/kg) compared with TSP (5.6g/kg) which would be expected to reduce P overland flow due to the additional sorption capacity of the organic matter in the granule. The higher concentration of Al and Fe complexes present in Duofos is also expected to have a significant effect on the solubility of P in the formulation. These effects may explain the slow release characteristics of Duofos compared with TSP. This is a key environmental advantage for Duofos especially following rainfall events. There were no significant differences in dry matter yield, soil P concentrations, plant leaf tissue or soil pH between Duofos and TSP at any of the treatment rates under either an intensive nitrogen (250 kg/ha N) or sustainable nitrogen (25 kg/ha N) regime.

Duofos may be recommended to reduce P concentrations in overland flow in grassland pastures and may have a particularly important environmental advantage in the period immediately following rainfall or during high rainfall periods.

CHAPTER 1

General Introduction

Phosphorus (P) has played an important role in raising agricultural productivity worldwide, but adverse environmental impacts associated with its past and current use on farmland are now becoming apparent in the developed countries as production methods have intensified and farming systems have become more specialised (Sharpley et al., 2005). P inputs to aquatic systems from agricultural runoff can be a major component of non-point source water pollution (Daniel et al., 1998). The application of organic and inorganic fertilizer in relation to rainfall events and soil water conditions have a considerable influence on P transfer through overland flow (Haygarth and Jarvis, 1997). Annual P losses from agricultural areas have been estimated to range from <1% to 32% of the P applied (Nash et al., 2000). The enrichment of fresh waters with nitrogen and phosphate has resulted in many fresh waters becoming more productive resulting in oligotrophic waters becoming eutrophic (Gibson, 1997). The critical threshold of P in freshwater above which eutrophication is likely to be triggered is approximately 0.03 mg/l of dissolved P and 0.1 mg/l of total P (Brady and Weil, 1996).

The trade name of Duofos is given to a fertilizer which is derived from naturally occurring Guano deposits. Physical properties and chemical composition of Duofos are outlined in table 1. These types of deposits occur in hot tropical regions where deposits from millions of sea birds have accumulated over tens of thousands of years. Locations around the world, Peru, islands off Africa, the Caribbean, and the Pacific Islands contain abundant guano reserves but there is no official record of world stock reserves. The Indonesian island of Madura located immediately north of the city of Surabaya on the mainland is the origin of the guano fertilizer used in this trial. It has an area of 4,560 km^2 and is densely populated with a population of 3.0154 million people in 1990.

Objectives

The main objectives of this research were to compare Duofos with Triple Superphosphate (TSP) in terms of:

Trial 1 (Chapter 2)

- A comparison of Duofos and Triple Superphosphate for phosphorus overland flow (mg/l)

Trial 2 (Chapter 3)

- A comparison of the effect of Duofos and Triple Superphosphate on grassland yield (kg/ha) under intensive (250kg/ha N) and sustainable (25kg/ha N) nitrogen regimes.

Table 1. 1 Physical properties and chemical composition of Duofos and Triple Superphosphate (TSP).

Characteristics	Duofos	Triple Superphosphate
Physical	Brown granules 3-4mm diameter	Grey granules 2-3mm diameter
Chemical content	**g/kg DM**	**g/kg DM**
Macro elements		
Phosphorus (P_2O_5)	220	380
Calcium (Ca)	100	194
Magnesium (Mg)	32	34.8
Potassium (K_2O)	37	0.95
Sulphur (S)	4	11.1
Aluminium oxide	60	0.75
Ferric oxide	40	1.88
Micro elements:	**mg/kg DM**	**mg/kg DM**
Molybdenum	10	1.74
Mercury	0.04	0.01
Cadmium	<4	8.89
Lead	<10	1.28
Total Phosphorus	**g/kg DM**	**g/kg DM**
	78	160
Organic carbon	86	5.6
Neutral Ammonium Citrate Solubility	7%	85%

Duofos data supplied by the manufacturer (P.T. Madura Guano) and TSP analysis was carried out by Frank Wright Ltd. (Laboratories), Derbyshire, UK.

CHAPTER 2

A comparison of Duofos and Triple Superphosphate for phosphorus overland flow (mg/l)

Introduction

Wallbrink et al. (2003) carried out a study quantifying the contributions of sediment-P and fertilizer-P from forested, cultivated and pasture areas at the catchment scale. At the catchment outlet, the amount of surface sediment eroded from cultivated lands was eighty-four times higher than that from pastures and the steep forested lands contributed nine times more than pastures. There was little contribution of sediment-P at the catchment scale from surface erosion of pastures. Concentrations of P were highest in 'storm event' suspended sediment samples taken from the pasture and cultivated areas. Fertilizer P may be transported-off land surfaces with sediments and they contribute to offsite sediment-P concentrations in some situations. However, the fertilizer contributions were episodic and variable and probably influenced by particle size as well as timing of fertilizer application with respect to subsequent rainfall amounts. Findings from a recent study in Ireland implicated soil type, flow regime and scale of the catchment area as the important factors when linking P transfer processes to catchment patterns and will be central to developing monitoring and migration strategies for managing P transfer to freshwater (Jordan et al., 2004).

Morgan's P soil test is the standard soil test in the Republic of Ireland as an indicator of soil P solubility and potential loss to water (Daly and Styles, 2005). An Irish study monitoring P losses from grassland identified a strong association between Morgan's P soil test and P concentrations in overland flow (Tunney et al., 2000). The concentration of P in overland and subsurface flow is related to the concentration and release rate of P in soil (McDowell and Sharpley, 2002). These authors reported that soil P release to solution was most likely controlled by a combination of Al, Fe and Ca complexes. Relative to the release of P, two processes appear to occur simultaneously, a rapid release of P from soil immediately in contact with the solution and a slower diffusion of P from inside soil aggregates. These processes should be considered when interpreting the release of P to overland and subsurface flow in soils of different P concentrations.

Soil P that accumulates beyond crop requirements is a major non-point source of agricultural P and high soil test P (STP) levels have been linked to losses in overland flow from grassland in Ireland (Kurz et al., 2005). The forms and the amount of P that is released due to overland flow depend on rainfall, soil conditions, the nature of the land surface and the amount and forms of P present. Soil particles suspended in water are an effective means of mobilising and removing P from an area. Erosion due to the impact of rainwater is increased by lack of crop cover, by topographical features that concentrate overland flow, by compacted tramlines and by rolling of late sown crops. Maintenance of a good topsoil structure and a reduction of the area of exposed soil surface, on the other hand, will combat erosion (Chambers et al., 2000).

Mixing of water and soil at the surface is mainly confined to the top 2 cm and is most intense in the top 1 cm of the soil (Sharpley et al., 1988). In a long-term grazing trial carried out at Teagasc Johnstown Castle, Ireland, over a period of twenty years Murphy and Culleton (2000) observed a stratification of available P in soil samples taken initially at 5mm depth and then at 20mm intervals down to a depth of 200mm with the larger concentrations found nearer the surface. In the zero P treatments (controls) there were 5.3 and 3.8 mg/l P in the top 0-5 and 5-100mm depths respectively while in the 30 kg/ha P treatment there were 51.8 and 18.7 mg/l P in the 0-5 and 5-100mm depths respectively. They concluded that the concentration of P in soil exposed to water flowing over the soil surface is therefore higher than would be indicated by tests on soil samples taken from 0-100mm as is the practice for grassland soils in this country. Mulqueen et al., (2004) suggested that in the absence of soil erosion, release of P from surface waters takes place from the surface 20 mm of soil and a good correlation was obtained by carrying out a Morgan's P test on samples taken from the top 20 mm of soil.

McGechan and Lewis (2002) described soil P as being contained in a number of 'pools', including dissolved inorganic P, inorganic P sorbed onto surface sites, inorganic P deposited by various slow time-dependant processes and various organic P pools. The quantity of each pool in a given time depends on the history of P fertilizer application, including the lapse of time since the most recent applications. The term 'labile P' is

commonly used to represent mobile P that is available as a nutrient for plant growth including soluble P and the P that is adsorbed onto soil surface sites. In common with other reactive chemicals, the extent to which P is adsorbed relative to P in solution is highly non-linear (McGechan and Lewis, 2002).

To determine if soluble P concentrations could be reduced in poultry litter Moore and Miller (1993) added various amounts of Al, Fe and Ca. They found that Ca added at a rate of 43 g/kg of litter reduced the soluble P concentration from >2000mg/kg to <1mg/kg. The soluble P was also reduced to <200mg/l and <100mg/l by the addition of 17g/kg Al and 35g/kg Fe respectively.

Sample et al. (1980) suggested that as the P solution moves away from the fertilizer granule site, the P concentration decreases by precipitation and dilution by soil water and a location in the soil is reached at which adsorption becomes dominant and precipitation negligible. As the fertilizer solution moves away from the granule into the soil, the displaced divalent and trivalent metal ions contribute to the concentration of soil-derived cations available for subsequent precipitation of P. Secondly, removal of the organic matter coatings on soil minerals may expose new surfaces which can participate in P adsorption. Thirdly, as the solubilized organic matter is carried to a new location in the soil it may precipitate, covering soil mineral surfaces that would otherwise have participated in P retention. Humus, since it is not negatively charged, is not thought to retain much P by itself in soils, however, in association with cations such as Fe^{3+}, Al^{3+}, and Ca^{2+} it is able to retain significant amounts (Wild, 1950). Moreno et al. (1960c) showed that organic matter may complex Ca ions and thus increase the P concentration in the soil solution from some of the Ca phosphates. Since the adsorption component of the fixation process is associated with the clay (<2µm) and hydrous oxide fractions, it follows that P retention will be greater in soils of higher clay content (Brady, 1990).

Many researchers view P retention as a continuum embodying precipitation, chemisorption and adsorption if the processes are viewed throughout the entire zone of soil influenced by a fertilizer application and through a time span encompassing an entire

growing season or longer (Sample et al., 1980). As highly-water-soluble fertilizers are applied to soils, the adjacent soil is bathed in solutions of very high concentrations of P and accompanying cations. It is in this environment that P retention reactions begin, not in the very dilute solutions commonly used to quantify sorption. Fertilizers are almost universally applied to soils having moisture contents appreciably below 'field capacity', primarily because this condition is desirable before spreading equipment is brought on to the land. Lawton and Vomocil (1954) found that the moisture content of granules of superphosphate (8% P) in a soil at >15 atmospheres (atm) moisture tension increased by 16.2% within 24 hours. Thus, ample moisture had moved into the granules to initiate dissolution. As water is drawn into this concentrated zone by vapour transport the fertilizer moves into the surrounding soil. The process of inward movement of water and outward movement of solution continues to produce a nearly saturated solution so long as any of the organic salt remains. This continues until the concentration is decreased by dilution or by reaction of fertilizer and soil constituents to the level at which no osmotic gradient exists (Huffman and Taylor, 1963).

Ammonium orthophosphate and polyphosphate fertilizers containing little or no Ca or micronutrient cations ordinarily dissolve completely in soils and leave no residues in the granule site (Khasawneh et al., 1974). The products formed in the initial stages of the reaction of soluble phosphate fertilizers with soils are metastable and with time will change into more stable and less soluble P compounds Some of them, however, may persist for sufficient time to act as a good source of P for plants (Sample et al., 1980). The inclusion of other fertilizer salts with these materials, however, may lead to in-situ precipitation. Successive increments of soil are contacted by the moving front of the fertilizer solution, encountering increasing amounts of Fe, Al, Mn, Ca, Mg and other soil-derived cations and the solution becomes supersaturated with respect to a variety of P compounds. These compounds slowly precipitate in the soil matrix. The nature of the precipitating compound depends on the kinds and amounts of cations and anions supplied by the fertilizer, the soil and by soil pH, and moisture.

Sample et al., (1980) suggested that the soil property most widely used to predict the ultimate products is pH, recognising that pH is itself a reflection of the degree of weathering, minerals present, exchangeable cations and a multitude of other factors. Lindsay and Moreno (1960) demonstrated that as a soil weathers with an accompanying decrease in pH, Ca phosphates are replaced by Al phosphates that in turn are replaced by Fe phosphates. Studies in soil residual P values on twenty-four sites throughout Britain by Larsen et al., (1965) showed that the only soil property found to be correlated with residual P availability was soil acidity.

Daly et al., (2002) in a study carried out on 35 river catchments in Ireland reported that poorly-drained soils produce greater amounts of overland flow and carry more P to surface waters compared with drier well-drained soils. Artificial sub-surface drainage and managing pastures to avoid compaction are known to reduce the incidence of overland flow (Turtola and Paajanen, 1995; Nguyen et al., 1998). Elevated levels of P in overland flow during summer are also thought to be caused by the accumulation of nutrients at the soil surface during dry periods (Dils and Heathwaite, 1996).

Objective

This trial was carried out to compare the differences in phosphorus concentrations in overland flow between an organic phosphorus fertilizer (Duofos) and a chemical phosphorus fertilizer, Triple Superphosphate (TSP), in a seven year pasture using rainfall simulators

Materials and Methods
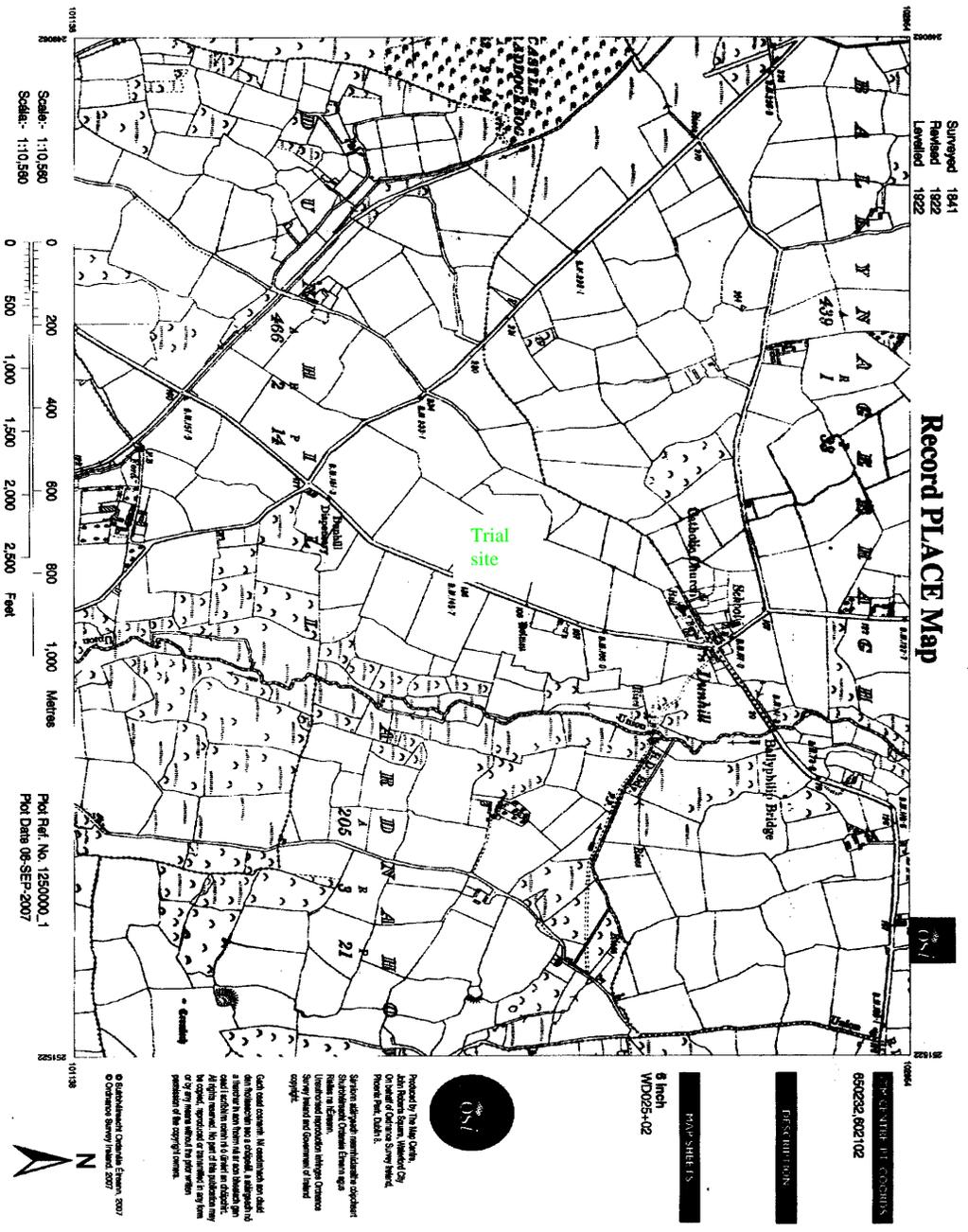
Figure 2. 1. Trial site location at Dunhill, Co. Waterford
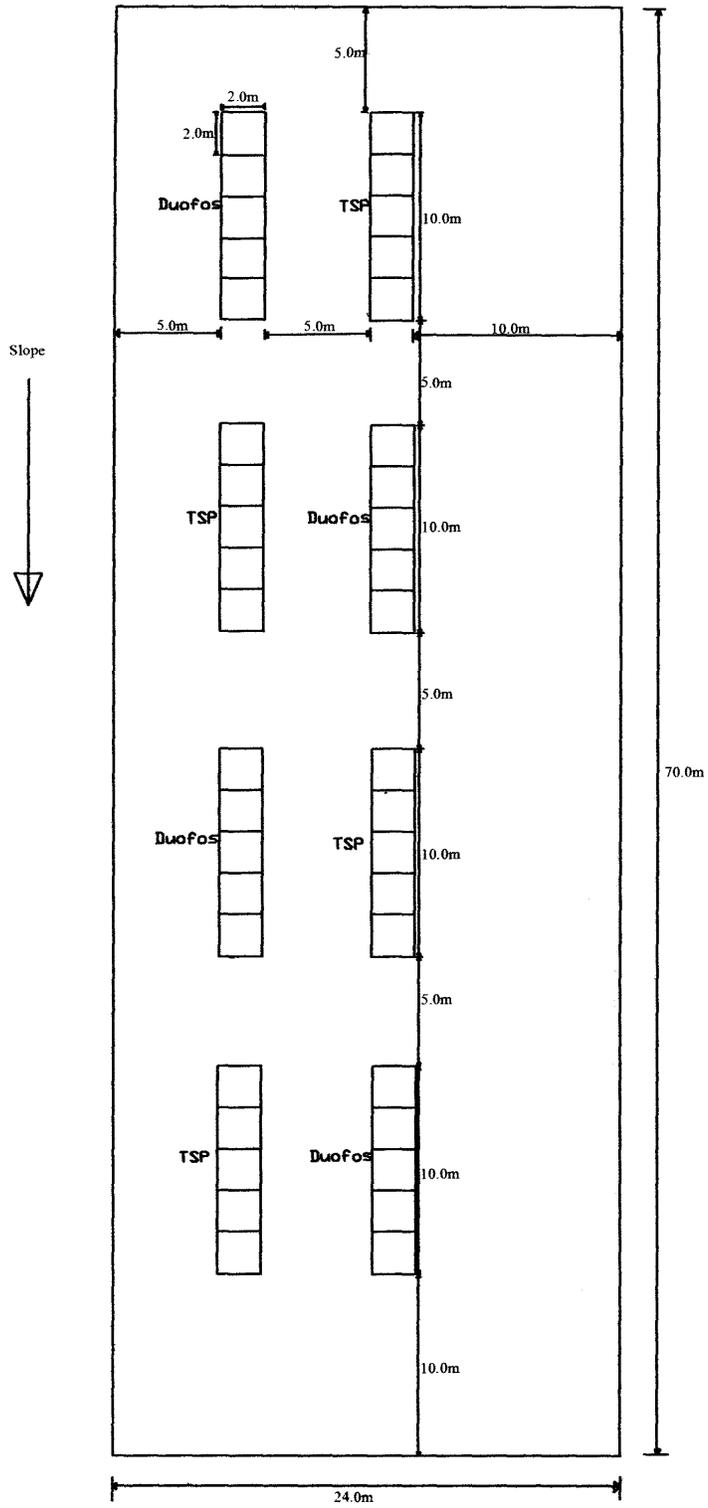
Figure 2. 2. Rainfall Simulator trial layout at
Dunhill, Co. Waterford

Location: Dairy farm of Mr. Anthony Murphy, Dunhill, Co. Waterford, Ireland

Site: Four sites were examined as potential trial sites but three of these sites had either artificial or organic P fertilizer applied in the previous six months which would have raised the soil P-index to 3 or higher (Teagasc 2004). The chosen site was a pasture for the previous seven years (preceded by two maize crops) with a gentle slope (1:20). No chemical or organic P fertilizer was applied for the previous six months on this site. Four replicated plots (10m x 2m) were marked out for each of the two treatments and fenced-off. Each plot was subdivided into five sub-plots (2m x 2m) to allow for randomisation of simulated rainfall applications at different dates (Figure 2. 2). Soil tests taken prior to the trial indicated that the site at 7.24mg/l was at the lower end of Index 3 (Morgan's soil P test).

Soil organic matter (Allen, 1989)

Soil was oven dried at 40^0C for 48 hours. Three 1g samples were weighed to four decimal places and organic matter content was determined by ashing for three hours at 600^0C. The soil samples were again weighed to four decimal places and reduction in weight calculated as the organic matter content.

Soil texture (Buurman et al., 1996)

Sixty soil cores were taken to a depth of 150mm from the chosen site in a W pattern (Teagasc, 2004) and mixed to form a compound sample. The samples were oven dried at 40^0C for 48 hours. The dried sample was filtered through a series of sieves with screen/mesh size ranging in descending order as follows: 2.000mm, 0.500mm, 0.250mm, 0.150mm, 0.100mm and 0.053mm. The samples at each measurement were weighed and recorded. After weighing, samples were re-mixed excluding material >2mm in preparation for removal of organic matter.

1. Organic matter removal.

100g samples of the sieved soil were placed in 250ml flasks and 50ml of deionised water was added. 50ml of hydrogen peroxide was gradually added in 10ml volumes and left to stand for 17 hours until the frothing had ceased The samples were then simmered on a hot plate, occasionally stirring and adding 5ml volumes of hydrogen peroxide until frothing had ceased 87 hours later. Contents were then washed through a 0.2mm sieve and a 0.053mm sieve with a fine jet of deionised water into a 1 litre graduated cylinder. The sand weight was calculated from the dried material from the 0.2mm sieve.

2. Silt and Clay Content.

The 1 litre cylinders containing the sieved material from the 0.053mm sieve was shaken for three minutes. A 22.9ml sample was withdrawn a distance of 10 cm from the surface of the liquid in the cylinder 47 seconds (at room temperature 18^0C) after shaking process was completed. The sample is transferred to an evaporating dish and dried at 105^0C and the dried contents weighed to give the weight of the silt plus clay.

3. Clay Content.

The process for silt content is repeated except the 22.9ml sample is withdrawn a distance of 7.5cm from the surface of the liquid 6 hours and 7 minutes after the initial shaking.

4. Silt.

The silt weight is then calculated by subtraction of the clay sample weight from the silt plus clay weight.

5. Soil pH.

Soil core samples were taken 10 cm depth using W patterns throughout the site and compound samples were analysed using a WTW TetraCon pH 340i meter with a Tetracon 325 probe attachment.

Treatments

Duofos and TSP were applied at 45 kg/ha phosphorus on June 27th 2004.

**Table 2. 1. Application rates (kg/ha) of Duofos and TSP to
achieve 45 kgs/ha of phosphorus**

Phosphorus	Duofos	Superphosphate
kg/ha	kg/ha	kg/ha
45	468.4	281.3

Simulated Rainfall

Simulated rainfall was applied at 35mm/hour using deionised water on the Duofos and Superphosphate plots simultaneously using two 'drip-type' simulators (Bowyer-Bower and Burt, 1989) which were based on a design supplied by the University of Amsterdam at the Laboratory of Physical Geography and Soil Science, and by the Agricultural Research Station Zaidin in Grenada. Water droplets are produced by 15mm lengths of 'Tygon' tubing (0.7mm internal diameter (ID), 2.3mm outside diameter (OD)) sealed into holes spaced at 30mm apart in a 1000mm x 500mm x 8mm perspex plate to form the base of a sealed perspex box when a similar non-porous perspex plate is bolted on top of a stainless steel frame of 8mm depth (appendix 3). The OD of the tubing determines the drop size created when water moves through the tubing (median drop size = 2.3mm). The ID of the tubing determines the rate of water drop formation. Water drop formation was further slowed by 25mm lengths of 0.55mm diameter nylon fishing line inserted through each tube. A fall height of 1.5m was achieved with this design. The flow rate of 35mm/hour was monitored and regulated by means of a valve which varied the volume of water flow from the reservoir overhead the unit to the droplet tubes.

Figure 2. 3 Rainfall simulator collection frame in situ July 2004

Due to the time constraints involved (approx 2 hours required per rainfall simulation, total 4 simulations/replicates for each treatment), it was necessary to carry out the two remaining simulations/replicates for each treatment on the following day (Table 2. 2). The same time constraints also made it impractical to include an untreated control.

Table 2. 2. Timings of simulated rainfall applications

and sample collection

Simulated Rainfall Application (35mm/hour)	Interval (days)	Days after fertilizer application
July 1-2nd	0	4-5
July 7-8th	6	10-11

| July 15-16th | 8 | 18-19 |
| July 21-22nd | 6 | 24-25 |
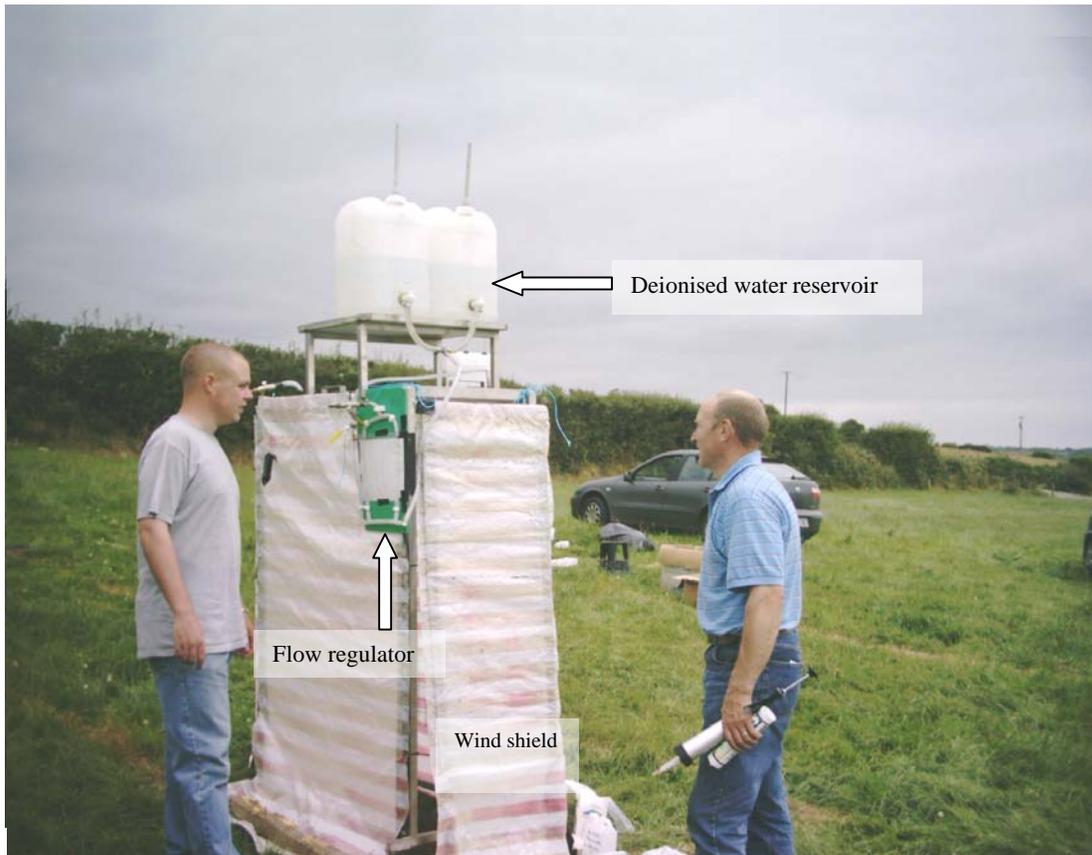
Figure 2. 4. Rainfall simulator on location July 2004

A sub-plot was randomly selected within each of the treatment plots by throwing a measuring tape across the plots and the sub-plot where it came to rest was used. Each sub-plot was used only once. The grass was cut to a height of approximately 1 cm using a hand clippers. A stainless steel frame (0.9m x 0.4m) was inserted in the soil and a trench (0.15m width x 0.4 m length x 0.2m depth) was dug at the end of the frame. Clear

Durabond silicon was applied between the inner wall of the frame and the soil to ensure a complete seal. Moist soil was also packed under the collecting trough to prevent any seepage of water (Figure 2. 3).

Soil moisture measurements were taken prior to each simulated rainfall application using a Delta-T HH2 Moisture Meter with attached ThetaProbe type ML2x with the display units option set to read in "mm Deficit".

Due to the high soil moisture deficit conditions prevailing during the period of the trial, 10 litres of deionised water was applied prior to each simulated rainfall application using a plastic watering can. The soil was then firmly tamped using a wooden block to reduce unevenness and create a compacted surface to reduce percolation and facilitate overland flow.

The rain simulator was prepared following the procedure described by Bowyer-Bower and Burt (1989) and following calibration it was placed over the soil frame and the rainfall applied at 35mm/hour (Figure 2. 4). Runoff was judged to be sufficient when water flowed through the collection spout at the rate of six droplets per minute. The runoff was then collected in plastic containers every ten minutes for one hour to give a total of six samples of runoff per treatment after each simulated rainfall (Figure 2. 5). Runoff samples in plastic containers were transported to the laboratory and stored at 4^0C.

A follow on trial was carried out in March 2005 to investigate longer term differences in DRP concentrations. After calibration the rainfall simulator was placed over the soil frame and the rainfall applied at 35mm/hour as per the previous trial in July 2004. The runoff was then collected in plastic containers, stored at 4^0C and analysed for phosphorus concentration using the Hach Spectrophotometer DR/2010.

Wind shield

Flow collection point with splash cover

Figure 2.5. Sample collection from rain simulator July 2004

Phosphorus analysis

Analysis of the runoff liquid for phosphorus compounds was carried out using a Hach Spectrophotometer DR/2010 (Table 2. 3).

Table 2. 3. Phosphorus compounds analysed in the overland flow samples and the analytical methods used with the Hach DR/2010 Spectrophotometer.

Phosphorus compounds analysed	Method
1. Dissolved reactive phosphorus	Molybdovanadate
2. Acid-Hydrolyzable phosphorus	Hydrolysis to dissolved reactive phosphate
3. Total phosphorus	Acid Persulfate Digestion

1. Dissolved reactive phosphorus

- A 25ml graduated cylinder was used to fill a sample cell with 25 ml of deionized water (the blank)
- A second 25 ml graduated cylinder was used to fill a second sample cell with 25 ml of sample (the sample)
- 1.0 ml of molybdovanadate reagent was added to each sample cell and hand swirled to mix.
- The blank was placed into the cell holder to zero the instrument
- The blank was removed and the prepared sample was placed in the cell and the results read in mg/l P

2. Acid-Hydrolyzable phosphorus

- A 25 ml sample was poured into a 50 ml Erlenmeyer flask using a 25 ml graduated cylinder
- 2.0 mls of 5.25N Sulphuric Acid was added using a 1.0 ml calibrated dropper
- The flask containing the prepared sample was placed on a hot plate and boiled gently for 30 minutes
- The sample was then allowed to cool to room temperature
- 2.0 mls of 5.0 N Sodium Hydroxide Solution was added using a 1.0 ml calibrated dropper and hand swirled to mix
- The prepared sample was poured into a graduated cylinder and deionized water rinsings from the sample container were used to return the volume to 25 ml
- A 25ml graduated cylinder was used to fill a sample cell with 25 ml of deionized water (the blank)

- A second 25 ml graduated cylinder was used to fill a second sample cell with 25 ml of sample (the sample)
- 1.0 ml of molybdovanadate reagent was added to each sample cell and hand swirled to mix.
- The blank was placed into the cell holder to zero the instrument
- The blank was removed and the prepared sample was placed in the cell and the results read in mg/l P

3. Total phosphorus

- A 25 ml sample was poured into a 50 ml Erlenmeyer flask using a 25 ml graduated cylinder
- The contents of one Potassium Persulphate Powder was added and hand swirled to mix
- 2.0 mls of 5.25N Sulphuric Acid was added using a 1.0 ml calibrated dropper
- The flask containing the prepared sample was placed on a hot plate and boiled gently for 30 minutes
- The sample was then allowed to cool to room temperature
- 2.0 mls of 5.0 N Sodium Hydroxide Solution was added using a 1.0 ml calibrated dropper and hand swirled to mix
- The prepared sample was poured into a graduated cylinder and deionized water rinsings from the sample container were used to return the volume to 25 ml
- A 25ml graduated cylinder was used to fill a sample cell with 25 ml of deionized water (the blank)
- A second 25 ml graduated cylinder was used to fill a second sample cell with 25 ml of sample (the sample)
- 1.0 ml of molybdovanadate reagent was added to each sample cell and hand swirled to mix.
- The blank was placed into the cell holder to zero the instrument
- The blank was removed and the prepared sample was placed in the cell and the results read in mg/l P

Granule solubility

25 grammes of Duofos and 25 grammes of TSP granules were placed in separate 250ml glass beakers and the beakers were filled to the 250ml mark with deionised water. The degradation of the granules was observed during the following hours (Table 2. 5).

Rainfall

Local rainfall was obtained from an Environmental Monitoring Station (Product No. 80652/2) supplied by ELE International and installed by the National Parks and Wildlife Service at Dunhill, Co. Waterford. Rainfall was recorded (mm/day) from June 28th to July 22nd 2004.

Statistical analysis

Excel 2003 (Microsoft 2003) was used for graphics and standard error analysis between treatments. The two-tailed t-test was used to test significant differences between Duofos and TSP treatments (Fowler & Cohen, 1990). SPSS – 13.0 software was used to carry out one-way analysis of variance (ANOVA) to compare treatments.

Results

Table 2. 4. **Soil properties**

Soil texture	Sandy
Sand	89.6%
Silt	8.6%
Clay	1.8%
OM	14.2%
pH	6.1

Table 2. 5. Granule solubility

	Duofos	TSP
Time required to dissolve granules in deionised water (minutes)	20	210
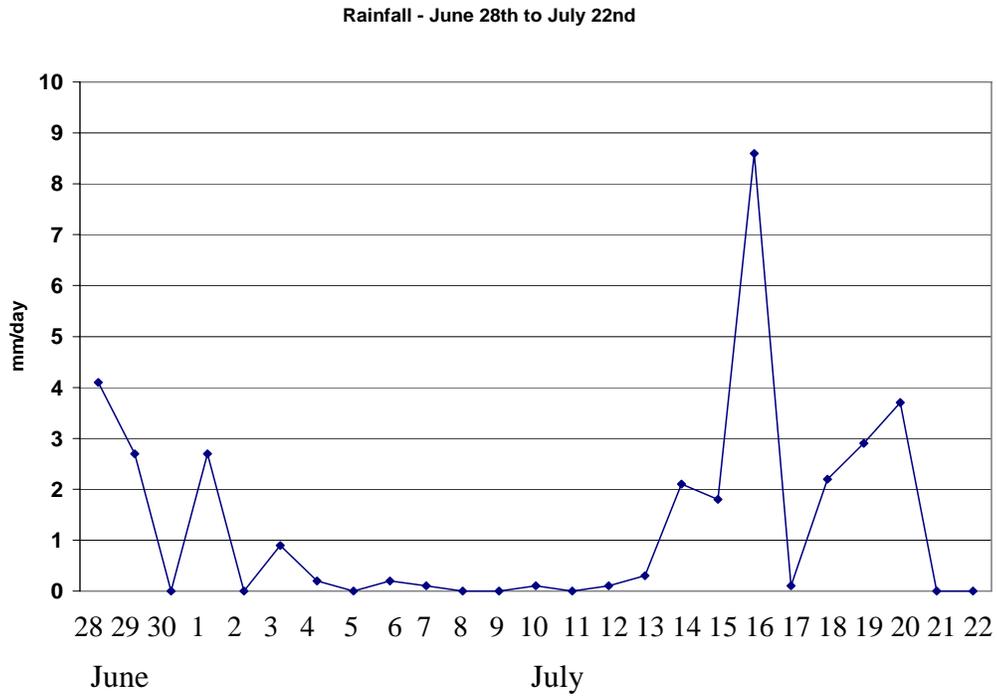
Figure 2. 6.   Rainfall recorded (mm/day) from June 28th to July 22nd at Dunhill, Co.
Waterford 2004

Table 2. 6. Soil Moisture readings

Dates	Soil moisture
July 1st	59mm deficit
July 2nd	52mm deficit
July 7th	23mm deficit
July 8th	27 mm deficit
July 15th	35mm deficit
July 16th	29 mm deficit
July 21nd	8mm deficit
July 22nd	9mm deficit

In this trial there were significantly lower (p<0.01) overland flow concentrations of dissolved reactive phosphate (DRP) in the case of Duofos compared with TSP on all sampling dates except the first sampling 4-5 days after P treatments (Figure 2. 7).

Dissolved Reactive Phosphate overland flow - July 2004
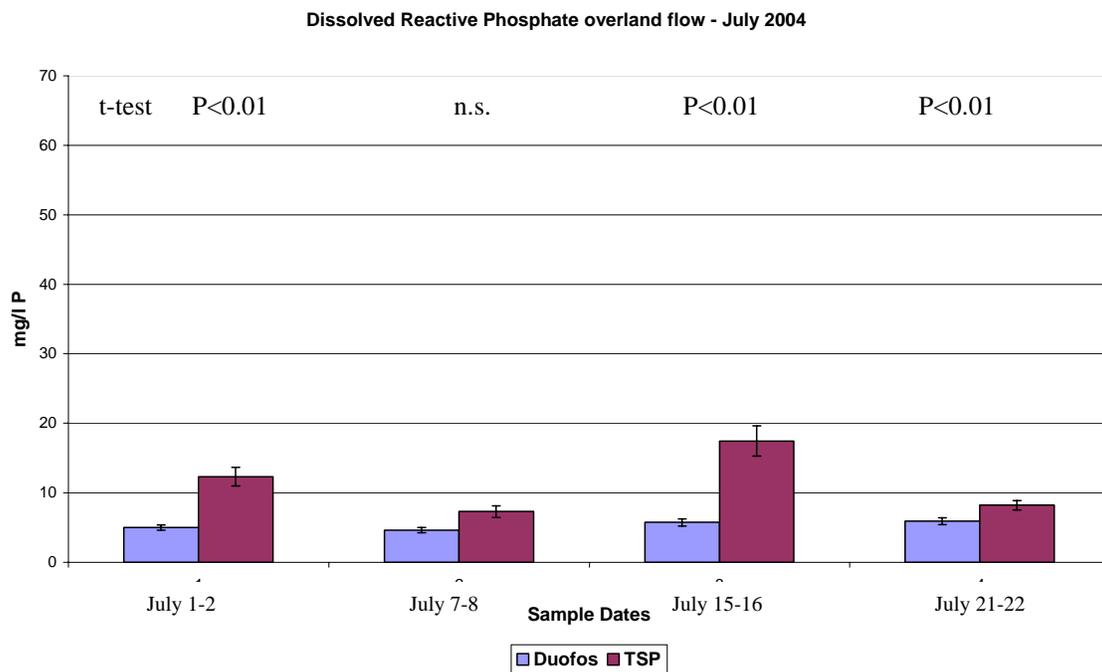
Figure 2. 7. Comparison of mean overland flow concentrations (mg/l) collected every 10 minutes for 1 hour for dissolvable reactive phosphorus on four sampling dates in July 2004.

Standard error confidence limits: p<0.05 with four replicates.

t-test: for differences in means of overland flow concentrations between treatments. n.s. = not significant

There were also significantly lower concentrations of acid-hydrolyzable P from the Duofos ($p < 0.01$, $p < 0.05$) on all sampling dates except on the second sampling (Figure 2. 8).

Acid hydrolyzable Phosphorus overland flow - July 2004
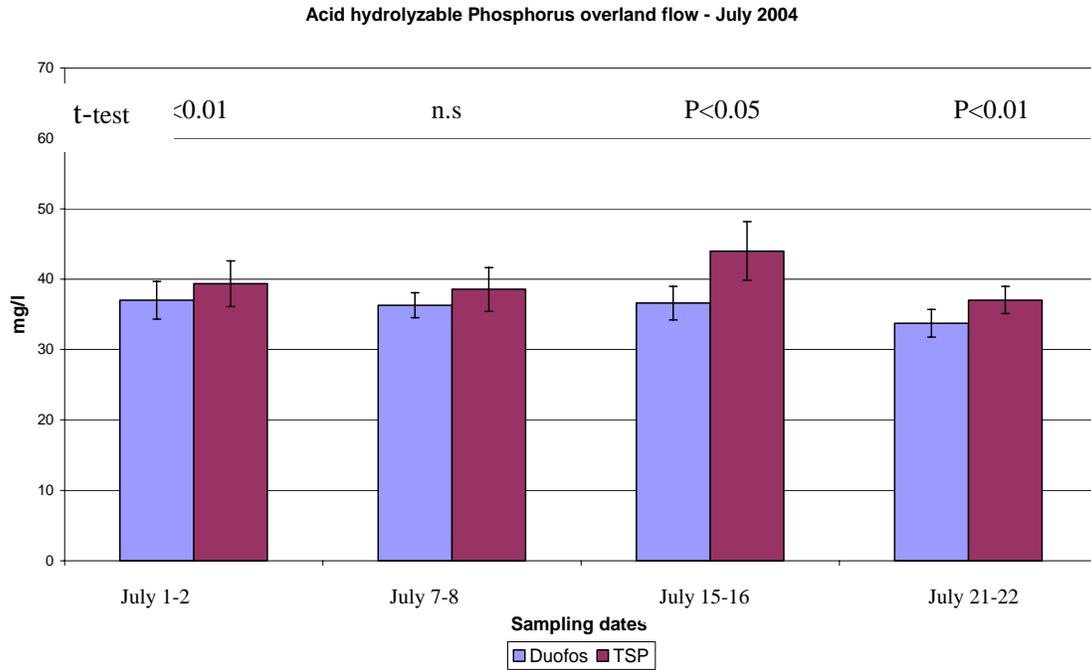
Figure 2. 8. Comparison of mean overland flow concentrations (mg/l) collected every 10 minutes for 1 hour for acid-hydrolyzable phosphorus on four sampling dates in July 2004.

Standard error confidence limits: $p < 0.05$ with four replicates

t-test: for differences in means of overland flow concentrations between treatments. n.s. = not significant.

There were significantly lower concentrations of total P from Duofos (p<0.02, p<0.01) on the two final sampling dates (Figure 2. 9).

Total Phosphorus overland flow - July 2004
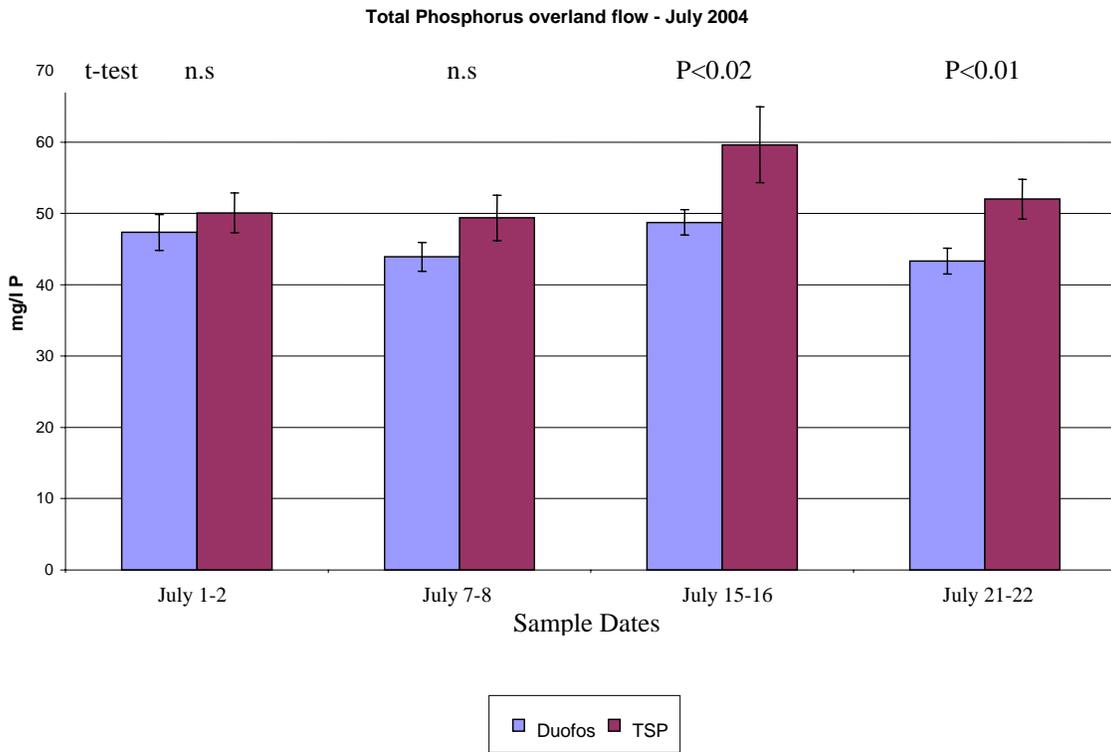
Figure 2. 9. Comparison of mean overland flow concentrations (mg/l) collected every 10 minutes for 1 hour for total phosphorus on four sampling dates in July 2004.

Standard error confidence limits: p<0.05 with four replicates.

t-test: for differences in means of overland flow concentrations between treatments.
n.s. = not significant

There were no significant differences between Duofos and TSP for overland flow concentrations of DRP from samples taken in March 2005 (Figure 2. 10).

Dissolved Reactive Phosphate overland flow - March 2005
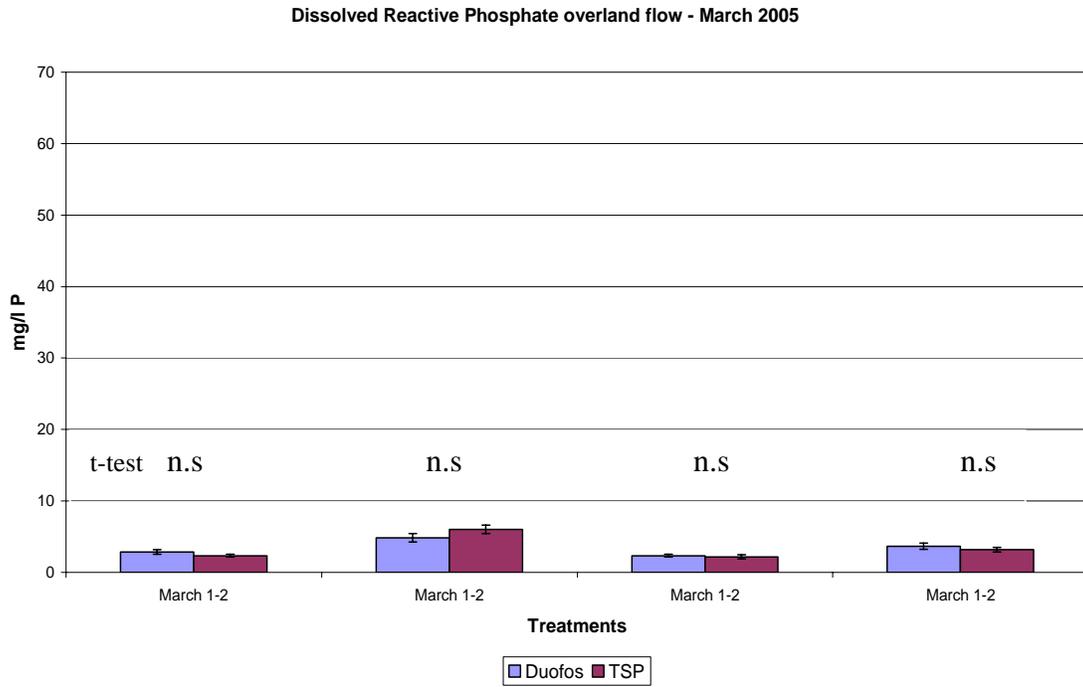
Figure 2. 10. *Comparison of mean overland flow concentrations (mg/l) collected every ten minutes for 1hour for dissolved reactive phosphorus.*

t-test: for differences in means of overland flow concentrations between treatments
n.s. = not significant

Discussion

Kurz (2002) described overland flow as being influenced by soil type, land cover and management, amount of rainfall, rainfall intensity, antecedent soil moisture, slope and artificial sub-surface drainage. The infiltration capacity is to a large degree determined by the texture, organic matter content and structure of a soil and soil structure can be weakened by low pH thereby further reducing infiltration capacity. The texture of the soil at this trial site is sandy which has relatively high percolation properties compared with e.g. clay soils. Some compaction of the surface of the soil was carried out to reduce penetrability and 10 litres of de-ionised water was added to each plot prior to each simulated rainfall application. Sharpley (1981b) reported that vegetation can lead to a decrease in the amount of particulate and/or dissolved P in overland flow. Reducing the vegetative cover on the trial plots by cutting the grass to 1 cm high was expected to increase the amount of P collected from overland flow due to increased availability of suspended solids.

In this trial there were significantly lower ($p<0.01$) overland flow concentrations of dissolved reactive phosphate (DRP) in the case of Duofos compared with TSP on all sampling dates except the first sampling 4-5 days after P treatments (Figure 2. 7). The first sampling coincided with a prolonged dry period and very high soil moisture deficit (Table 2. 5). There were also significantly lower ($p<0.05$) concentrations of acid-hydrolyzable P from the Duofos on all sampling dates except from the second sampling (days 10-11 after P treatment) (Figure 2. 8). There were significantly lower concentrations of total P from Duofos on the two final sampling dates (18-19 days and 24-25 days respectively, after P treatment) (Figure 2. 9).

As DRP, and to a lesser extent acid-hydrolyzable phosphorus, present a major risk of eutrophication of surface water bodies, the significantly lower concentrations of these P compounds in the case of Duofos compared with TSP is a major environmental advantage (Figure 2. 7, Figure 2. 8). The concentration of phosphorus in overland and subsurface flow is related to the concentration and release rate of P in soil, (McDowell and Sharpley, 2002). These authors reported that soil P release to solution was probably controlled by a combination of Al and Fe complexes. Sample et al (1980) concluded that

there is a positive relationship between the organic matter content of soils and P adsorption and that these relationships probably reflect the association of organic matter with cations such as Fe^{3+}, Al^{3+} and Ca^{2+}. Clays saturated with these trivalent ions adsorb more P than clays saturated with monovalent ions. The organic matter content of the soil at the trial site was 14.2%. This is above average and would be expected to reduce the P overland flow in the case of both Duofos and TSP. In addition Duofos had a significantly higher organic matter content of 86 g/kg compared with TSP (5.6 mg/kg) which would be expected to reduce P overland flow even further due to the additional sorption capacity of the organic matter in the granule (Table 1. 1). The higher Al and Fe are expected to have had additional effects on the solubility of P in the formulation. These combined effects may explain the slow release characteristics of Duofos. This would support research carried out by Moore and Miller (1993) when they demonstrated the significant effects of Al and Fe in reducing the solubility of P in chicken manure.

Overland flow of phosphorus as a result of rainfall events following the application of organic and inorganic fertilizer has a considerable influence on P transfer to water bodies (Haygarth and Jarvis, 1970). The trial at Teagasc Johnstown Castle where artificial P fertilizer was applied over a period of 30 years, demonstrated that P is concentrated mainly in the top 0-5mm of soil (Murphy & Culleton, 2000).

The soil moisture deficit at the trial site was 35mm and 29mm on July 15th and 16th respectively (Table 2. 5). The 8.7mm rainfall recorded on July 16th and a further 9mm over the following 5 days reduced the soil moisture deficit to 8mm on July 21st. The sandy texture of the soil would have contributed to the relatively slow reduction in the soil moisture deficit

A granule solubility test (Table 2. 5) using deionised water showed that the Duofos granules had totally degraded in 20 minutes compared with 210 minutes for the TSP. This indicates that the Duofos granule has considerably less physical stability than TSP. The ammonium citrate solubility of the TSP was 85% (i.e. 85% available P) compared with 7% for Duofos (Table 1. 1). The much greater differences in granule solubility and

34

ammonium citrate solubility in the case of TSP is likely to account for the peak in P overland flow for this fertilizer on July 15th-16th after the heavy rainfall.

In the event of rainfall the risk of overland flow is expected to be high after a recent application of a soluble fertilizer such as TSP (Figure 1. 1). Following a period of 18-19 days after phosphate treatments (15th & 16th July) at the Dunhill site, high overland flow concentrations of DRP (Figure 2. 7), acid-hydrolyzable P (Figure 2, 8) and total P (Figure 2. 9) were recorded in the case of TSP. This data was recorded following 48 hours of rainfall inn the trial area (Figure 2. 6).

This sudden peak of P release on the soil surface could potentially pose a high risk to pulse or flash pollution of phosphorus to waterways. The lower concentrations of phosphorus collected from the Duofos treated plots indicate a much lower mobilization of phosphorus during and after heavy rainfall. This is another very important environmental advantage for Duofos over TSP especially in the relatively high rainfall Irish climate.

A follow-on trial of P concentrations in overland flow carried out in March 2005 to investigate longer term differences in DRP concentrations did not result in any significant difference between treatments (Figure 10. 2). The residual concentrations of DRP in the overland flow measurements were low in the case of both TSP and Duofos treatments indicating residual losses of P from both formulations over winter 2004-2005. This confirms that the greatest risk of P loss is in the weeks immediately following application of P fertilizer. As the most significant result for phosphorus concentration in overland flow was found in DRP, only this trial was followed up in 2005 due to time and resource limitations.

CHAPTER 3

A comparison of the effect of Duofos and Triple Superphosphate on grassland yield (kg/ha DM) under intensive (250kg/haN) and sustainable (25kg/haN) nitrogen regimes

Introduction

Phosphorus in DNA is involved as a carrier of genetic information and in RNA as part of the structure responsible for the translation of the genetic information. The proportion of phosphorus in nucleic acids to totally organically bound phosphorus differs between tissues and cells. It is high in meristems and low in storage tissue. Phosphate esters and energy rich phosphates represent the metabolic machinery of the cells. Most phosphate esters are intermediates in metabolic pathways of biosynthesis and degradation. Their function and formation are directly related to the energy metabolism of the cells and to the energy rich phosphates. Required energy for ion uptake is supplied by energy rich coenzymes, principally ATP (adenosine triphosphate).

In many enzyme reactions P is either a substrate or an end product (e.g. ATP -> ADP + P). P controls some key enzyme reactions. Compartmentation of P is therefore essential for the regulation of metabolic pathways in the cytoplasm and the chloroplasts (Marschner, 2003). In leaves of phosphorus-deficient plants virtually all P is found in the cytoplasm and chloroplasts, i.e. in the 'metabolic pool' (Foyer and Spencer, 1986). Typically, under phosphorous deficiency, shoot growth is much more depressed than photosynthesis.

The phosphorus requirement for optimal growth is in the range 0.3 – 0.5% of the plant dry matter during the vegetative stage of growth (Marschner, 2003). In plants suffering from phosphorus deficiency reduction in leaf expansion and leaf surface area and also number of leaves are the most striking effects (Fredeen et al., 1989; Lynch et al., 1991). Leaf expansion is strongly related to the extension of epidermal cells and this process might be particularly impaired in phosphorus-deficient plants for various reasons, e.g. low phosphorus content of epidermal cells and decreases in root hydraulic conductivity (Treeby et al., 1987; Radin, 1990). In contrast to the severe inhibition in leaf expansion, the contents of protein and of chlorophyll per unit leaf area are not much affected (Rao and Terry, 1989). Often, the chlorophyll content is even increased under phosphorus deficiency and leaves have a darker green colour as cell and leaf expansion are more

37

retarded than chloroplast and chlorophyll formation (Marschner 2003). However the photosynthetic efficiency per unit of chlorophyll is much lower in phosphorus deficient leaves (Lauer et al, 1989b).

In contrast to shoot growth, root growth is much less inhibited under phosphorus deficiency, leading to a typical decrease in the shoot-root dry weight ratio (Freeden et al., 1989). As a rule, the decrease in shoot-root dry weight ratio in phosphorus deficient plants is correlated with an increase in partitioning of carbohydrates towards the roots, indicated by a steep increase particularly in sucrose content of the roots of phosphorus deficient plants (Khamis et al., 1990a). Phosphorus deficiency might even enhance elongation rate of individual root cells and of the roots (Anuradha and Marayanan, 1991). Despite these adaptive responses in increasing phosphorus acquisition by roots, not only is shoot growth retarded by phosphorus limitation but the formation of reproductive organs is also inhibited. Flower initiation is delayed (Rossiter, 1978), the number of flowers decreased (Bould and Parfitt, 1973), and seed formation is restricted (Barry and Miller, 1989). Premature senescence of leaves is another factor limiting seed yield in phosphorus-deficient plants (Marschner, 2003).

Ozanne (1980) outlined the results of an experiment where three grass species were in culture solutions containing five levels of P ranging from 0.003 ppm to 30.0 ppm. Large yield responses were obtained in all three species and total P taken up was related to yield rather than to the concentration in the tissue. The major factor determining P uptake appeared to be the demand of the above ground vegetation or its ability to dilute absorbed P through photosynthesis and growth. The level of P in the culture solution required for 90% of maximum yield of a particular species was related to the ability of the roots to absorb and translocate P rather than the ability of the above ground vegetation to function at a lower internal P concentration.

Luxury P uptake by plants does not occur to any great extent (Sharply *et al*, 1994b). Where soil-P levels are high the rate of uptake of P does not increase proportionally but approaches a maximum (Asher and Lonergan, 1967). Following a major survey of Irish

farm soils Culleton et al (1996) concluded that some 20% of the soils analysed for nutrient status had P levels in excess of 10mg/l (Morgan's P soil test), and that these concentrations are unnecessary for optimum production. Carton et al. (2005) published results on low P index soils (P index 1) where a positive yield response was achieved in wheat. Murphy and Culleton (2000) reported that maximum beef production took place with a soil Morgan's P test of 6mg/l. Schulte et al. (2006) reported that increasing plant P tissue content to 0.3 mg/l required higher soil test P than what would be required to achieve maximum yield. As the baseline soil P recorded at the start of this trial was 7.24 mg/l, which is Index 3 according to the Teagasc Soil Index System, the response to P fertilizer was labelled as 'unlikely/tenuous', and therefore a yield difference between treatments was unlikely.

By definition, the maintenance requirement of phosphorus in animals is the faecal loss when phosphorus supply is just below or just meets the true requirement. Typically 95 to 98% of total phosphorus excretion is in faeces (NRC 2001). Dairy cattle are quite adept at excreting excess absorbed phosphorus to maintain concentrations of phosphorus in the blood within a normal range (5-6 mg/100ml) via secretion of saliva which contains varying amounts of phosphorus (depending on blood P concentrations) through the salivary glands which mixes with the food in the digestive tract and is then reabsorbed or lost via faecal excretion. Hartmann et al. (1995) reported that intensive animal husbandry in the light sandy loamy soils in Flanders resulted in an overproduction of manure. In this situation phosphorus (P) input exceeded P requirements for crop production resulting in P accumulation in the soil.

Objectives

This trial was carried out to investigate if there was significant differences between Duofos and TSP in dry matter (DM) yield, plant tissue P concentration and soil pH effect at two nitrogen regimes, intensive nitrogen (250 kg/ha N) and sustainable nitrogen (25 kg/ha N).

Materials and Methods

A trial site was fenced off in a long-term pasture immediately adjacent to the site used for the overland flow trial in Dunhill, Co. Waterford (Figure 3. 1). The site was divided into two adjoining sub-sites (Figure 3. 2) with two different nitrogen regimes; intensive (250 kg/ha N) nitrogen and sustainable (25 kg/ha N) nitrogen (Table 3. 1). The low rate of nitrogen applied on the sustainable sub-site was designed to encourage the spread of clover and thus supply nitrogen naturally.

Table 3. 1. Intensive and sustainable nitrogen applications 2004

Sub-site	A	B
	Intensive kg/ha N	Sustainable kg/ha N
March 17	100	25
May 6	80	--
June 12	60	--
July 31	10	--
Total kg/ha	**250**	**25**

Plots (5m x 1m) were marked out in a randomised block design with five replicates per treatment (Figure 3. 2). Seven treatments were applied including a control treatment (Table 3. 2) **Duofos** (22% P_2O_5) and **Triple Superphosphate** (40% P_2O_5) were applied at different application rates on March 10th (Table 3. 2). Control plots did not receive any phosphorus application.

Record PLACE Map

Surveyed 1841
Revised 1922
Levelled 1922

Scale:- 1:10,560
Scale:- 1:10,560

0 200 400 600 800 1,000 Metres

0 500 1,000 1,500 2,000 2,500 Feet
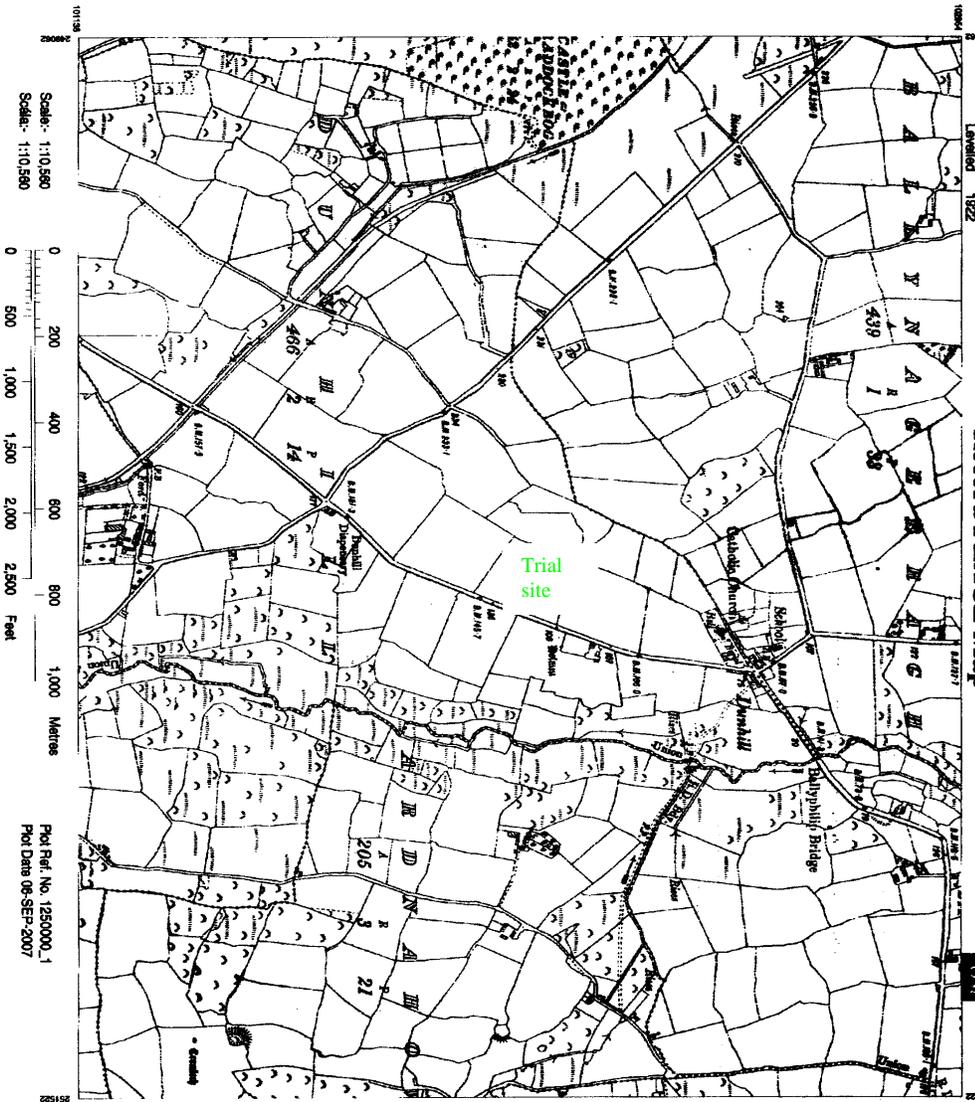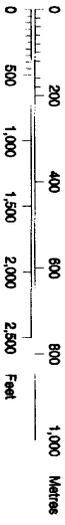
Plot Ref. No. 1250000_1
Plot Date 06-SEP-2007

Trial site

CASTLE CUFFOGUES

BALLYNAGEE

REDMONDSTOWN

Ballyphilip Bridge

Catholic Church

Schools

439

466

205

N

Figure 3. 1. Trial site location at Dunhill Co. Waterford

Intensive N treatments

Sustainable N treatments
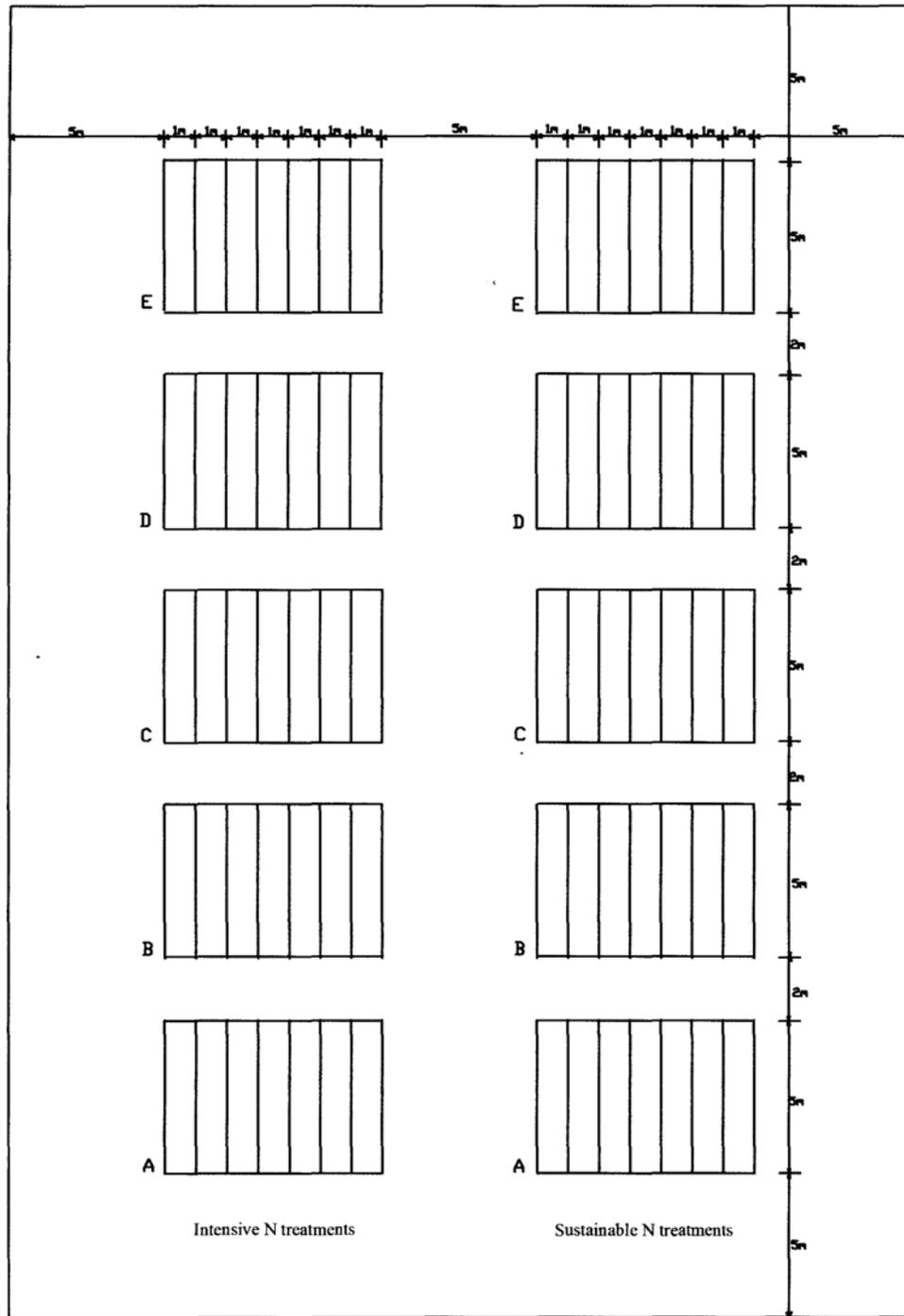
Figure 3. 2. Trial site layout for Intensive and
Sustainable Nitrogen regimes

E

E

C

E

Row A

5m x 1m plot

Figure 3. 3. Grassland trial with intensive (250 kg/ha N) and sustainable (25kg/haN) nitrogen regimes at Dunhill, Co. Waterford 2004.

Table 3. 2. Duofos and TSP treatments with applied phosphorus concentrate (kgs/ha)

		Duofos (kg/ha)	TSP (kg/ha)	Phosphorus (kg/ha)
1	Duofos	156.2	-	15
2	Duofos	312.3	-	30
3	Duofos	468.6	-	45
4	TSP		93.8	15
5	TSP		187.5	30
6	TSP		281.3	45
7	Control	-	-	-

An overall base dressing of **Potash** was applied on two dates on both trials (Table 3. 3.) to eliminate the possibility of a K deficiency.

Table 3. 3. Base dressing of Potash applied overall

Date	Kg/ha K
March 17th	80
June 12th	80

Yield (kg/ha DM)

The plots were harvested four times during the growing season (Table 3. 4.).

Table 3. 4. Harvest dates 2004

Month	Date
May	3rd
June	10th
July	28th
September	9th

A Raleigh ride-on mower with 90cm cutting width and two solid grass collecting boxes was used for harvesting. Areas surrounding the plots were cut on each occasion at 2 cm height on the day preceding harvest to ensure no excess grass was collected from the areas immediately outside the plots. The plots were then cut the following day at 3 cm height. The grass was transferred from the collection boxes into plastic bags and weighed on site using a Salter Electro Samson balance (range +/- 0.01kg). Samples of grass were taken from four locations within the plastic bags, placed in plastic ziplock bags and the air was partially removed for ease of transport and storage. The grass was stored in the Ziploc bags at 4^0C in a refrigerator.

During the following week the grass samples were removed from the refrigerator and 200 grams of each sample was weighed to three decimal places on a pan balance. The samples were then dried in an oven at 80^0C for 24 hours and the dried vegetation was re-weighed. The percentage dry matter was then calculated for each sample.

Plant tissue P (mg/l)

Plant tissue P analysis was carried out following the procedure reported by Pinevich et al (1959) as follows:

Dried samples were ground down to a fine powder using a glass bowl in preparation for plant tissue analysis using the Sulphuric acid-hydrogen peroxide procedure. A digest

consisting of sulphuric acid (conc.), hydrogen peroxide (30%), selenium powder, lithium sulphate monohydrate (purest available grade) was prepared as follows:

350ml of H_2O_2, 0.42g Se and 14g $LiSO_4$ was added to a one litre boiling flask and 420ml of H_2SO_4 was gradually added over a period of one hour as considerable heat was generated with each acid addition. 4.4mls of this digest was added to 0.3g of oven dried (80^0C) ground grass leaf tissue sample and heated gently to initiate a chemical reaction. Gentle heat was continued until the digest was clear.

Soil pH

Soil pH analysis was carried out following the procedure reported by Peech et al (1944) as follows:

Soil samples were taken (20 cores of 10cm deep in a W pattern outlined in Teagasc 2004 from each 5m x 1m plot) from both the intensive nitrogen treated and the sustainable nitrogen trials after the fourth harvest in September 2004. pH analysis was carried out using a WTW 340i pH meter with a WTW TetraCon 325 probe attachment.

Soil samples were oven dried at 40^0C in a ceramic crucible for 24 hours. The dried samples were brushed through a 2mm mesh sieve. A 10ml volume of the dried sieved soil was mixed with 20ml of deionised water. Samples were stirred with a glass rod and allowed to stand for 10 minutes. pH was measured using the above meter.

Further soil samples were taken from the intensive nitrogen treated plots only (20 cores of 5mm deep in a W pattern as outlined in Teagasc 2004 from each 5m x 1m plot) also in September 2004 to investigate if a potentially higher concentration of applied fertilizer (Murphy & Culleton, 2000) had an influence on pH.

Soil P (mg/kg)

Soil P analysis was carried out following the procedure reported by Peech et al (1944) as follows:

Soil samples taken in March prior to P treatment (baseline) and after harvest 4 in September 2004 (treated samples) were analysed for P using the Morgan's Extracting Solution (Morgan, 1939).

Morgan's Extracting Solution.

Morgan's Extracting Solution was prepared for soil sample analysis as follows:

400g of 40% NaOH (Analar grade) was dissolved in 1 litre of deionised water. 350mls of this solution was mixed with 3.75 litres of deionised water and 360mls of glacial acetic acid. The total mixture volume was increased to 5 litres and the pH adjusted to 4.8.

An 8ml volume of soil was mixed with 40mls of Morgan's Extracting Solution in a round bottomed shaking flask and were shaken for 30 minutes on a mechanical shaker. The suspension was then filtered throughn Whatman 2 filter paper into a 50ml beaker. The filtration was then ready for P analysis.

Statistical analysis

Excel 2003 (Microsoft 2003) was used for graphics and standard error analysis between treatments. SPSS – 13.0 software was used to carry out one-way analysis of variance (ANOVA) to compare treatments.

Results

There were no significant differences in dry matter (DM) grass yield (kg/ha DM) ($p < 0.05$) between Duofos and TSP at any of the treatment rates in either the intensive or the sustainable nitrogen trials (Figures 3, 4 & 3. 5).

Intensive Grass Yields (kg/ha DM) Dunhill 2004
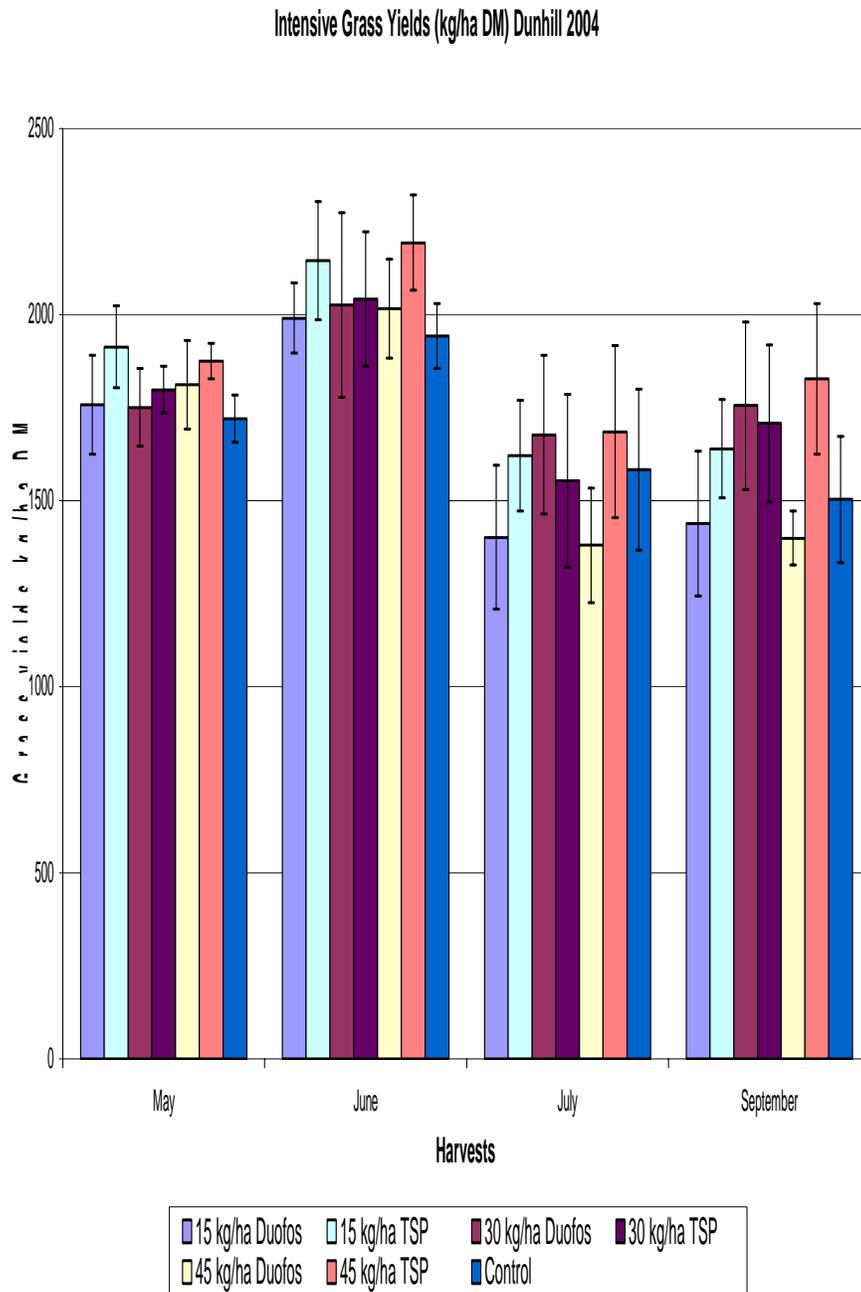
Figure 3. 4. Mean grass dry matter (DM) yield (kg/ha DM) per treatment from intensive nitrogen regime from four harvests during 2004. Standard error confidence limits : $p < 0.05$ with five replicates.
One-way analysis of variance show no differences between treatments for ($p < 0.05$) for each of the harvests.

Table 3. 5. Analysis of variance results for Duofos vs TSP. The dependent variable is dry matter (DM) yield. Results are presented for May, June, July and September harvests 2004, for each of two nitrogen regimes.

		Sum of Squares	df	Mean square	F	Sig.
Harvest 1 Intensive May	Between Groups Within groups Total	145814.6 1307206 1453020	6 28 34	24342.435 46685.924	.512	.788
Harvest 2 Intensive June	Between Groups Within groups Total	232846.6 3391210 3624048	6 28 34	38807.769 121114.331	.320	.921
Harvest 3 Intensive July	Between Groups Within groups Total	456129.9 5660150 6116280	6 28 34	76021.649 202148.215	.376	.888
Harvest 4 Intensive September	Between Groups Within groups Total	817978.8 4502517 5320496	6 28 34	136329.806 160804.187	.848	.544
Harvest 1 Sustainable May	Between Groups Within groups Total	153969.6 1832754 1986724	6 28 34	25661.600 65455.517	.392	.878
Harvest 2 Sustainable June	Between Groups Within groups Total	24161.099 1017260 1041421	6 28 34	4026.850 36330.701	.111	.994
Harvest 3 Sustainable July	Between Groups Within groups Total	139194.6 606954.5 746149.1	6 28 34	23199.094 21676.947	1.070	.404
Harvest 4 Sustainable September	Between Groups Within groups Total	193448.2 2686478 2879926	6 28 34	32241.365 95945.637	.336	.912

Sustainable Grass yields (kg/ha DM) Dunhill 2004
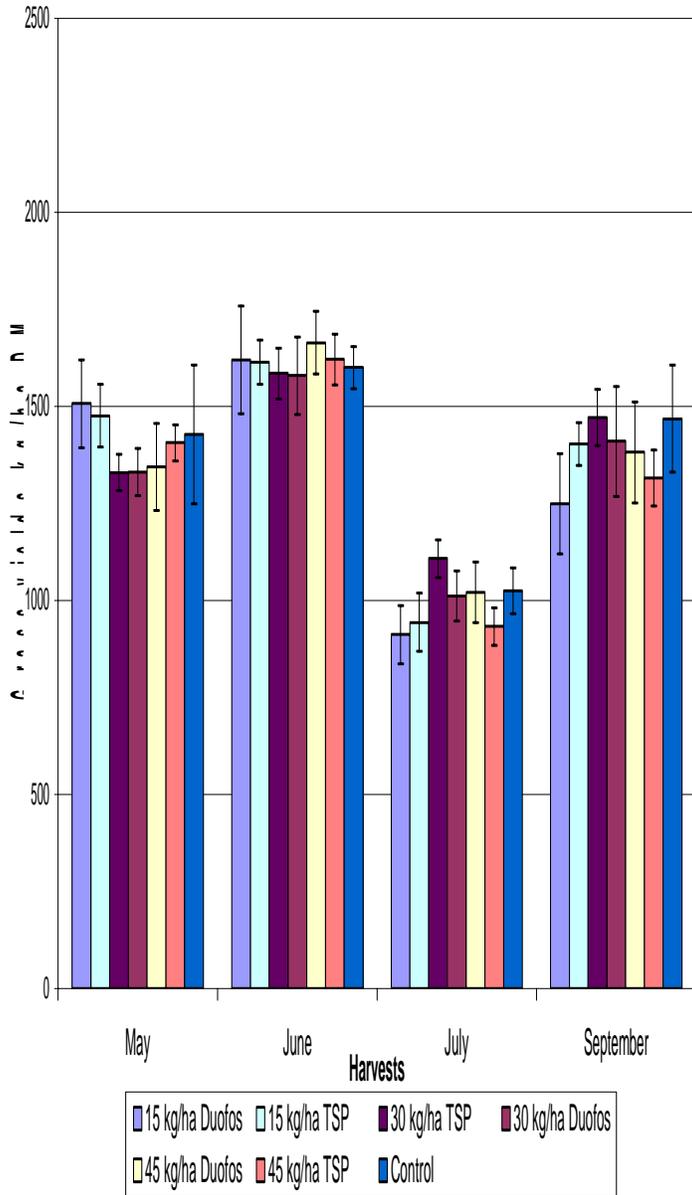
Figure 3. 5. Mean grass dry matter (DM) yield (kg/ha DM) per treatment from sustainable nitrogen regime from four harvests during 2004. Standard error confidence limits : p < 0.05 with five replicates.
One-way analysis of variance show no differences between treatments for each of the harvests.

Plant leaf samples analyzed for P concentrations did not reveal any significant difference (p<0.05) between Duofos or TSP at any of the treatment rates in either the intensive or the sustainable nitrogen trials (Figure 3. 6).
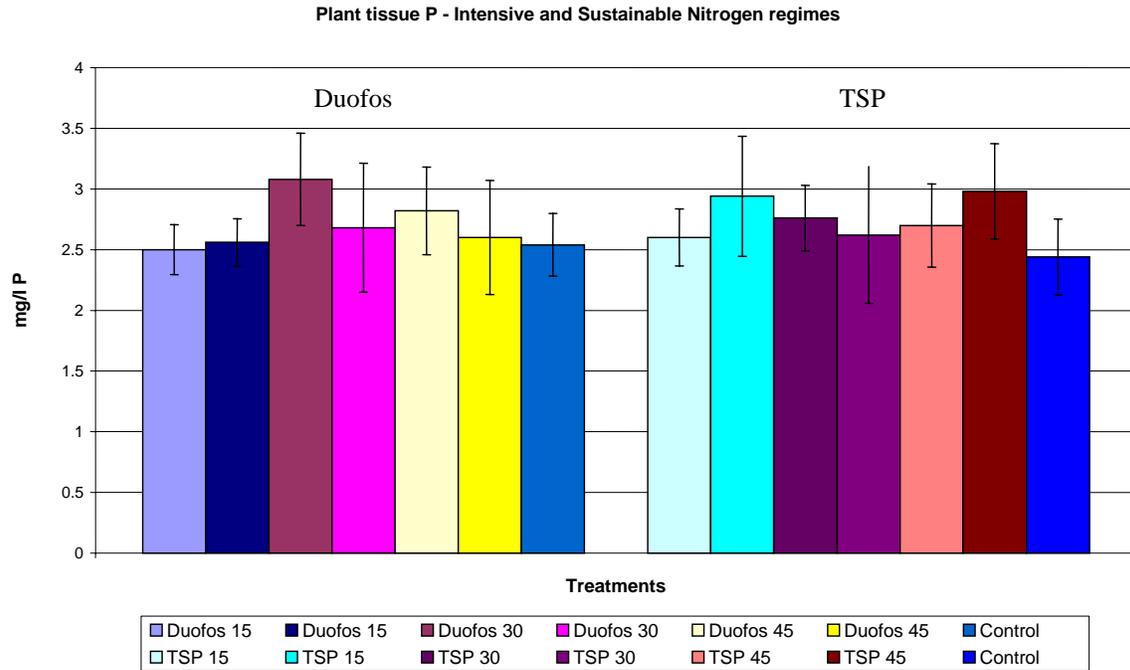

Figure 3. 6. Mean concentrations of phosphorus in plant leaf tissue (mg/kg) from samples taken from intensive and sustainable Nitrogen regimes in September 2004.

Standard error confidence limits: p < 0.05 with five replicates.

One-way analysis of variance show no differences between treatments in either nitrogen regime.

Table 3. 6 Analysis of variance results for Duofos vs TSP. The dependent variable is difference (intensive – sustainable) in plant tissue P.

		Sum of Squares	df	Mean square	F	Sig.
Duofos vs TSP	Between Groups Within groups Total	2.155 39.392 41.547	6 28 34	.359 1.407	.255	.953

There were no significant differences (p<0.05) in soil P concentrations between baseline (B) samples taken in March 2004 and post-treatment sustainable (S) samples taken in September 2004 for any of the treatment rates of either Duofos or TSP under the intensive or sustainable nitrogen regimes (Figure 3. 7).

Morgan's soil P (mg/l) Baseline v Sustainable Nitrogen regimes for Duofos and TSP
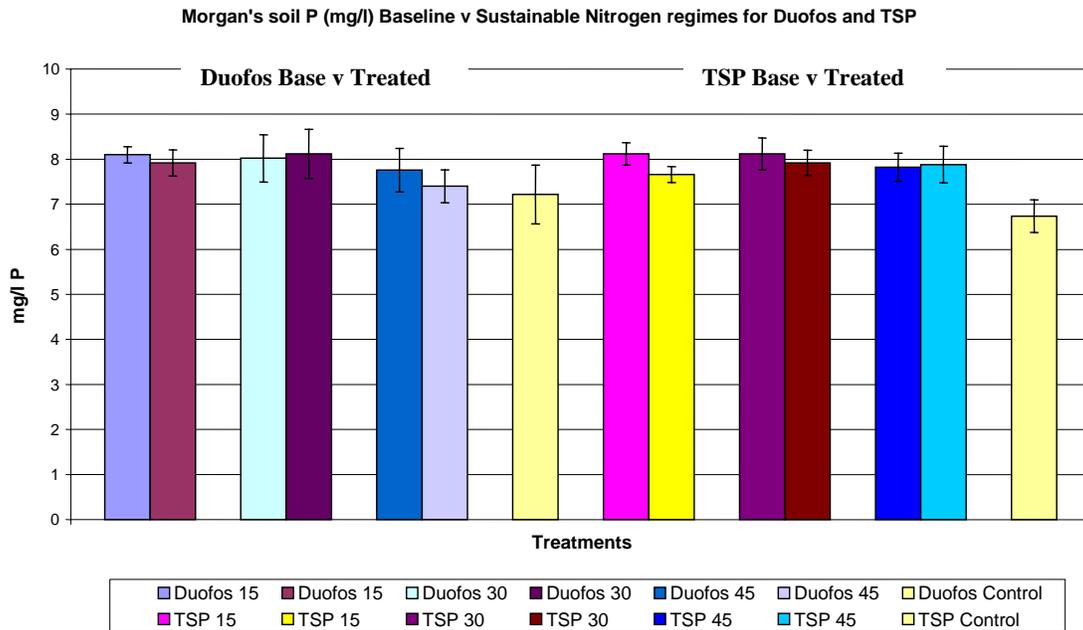
Figure 3. 7. Mean Morgan's soil phosphorus of samples taken from sustainable Nitrogen regime in September 2004.

Standard error confidence limits: p < 0.05 with five replicates.

One-way analyses of variance show no differences between treatments in either regime.

Table 3. 7 Analysis of variance results for Duofos vs TSP, under a sustainable nitrogen regime. The dependent variable is differenc (baseline – treated) in Morgan's soil P concentration.

		Sum of Squares	df	Mean square	F	Sig.
Duofos vs TSP	Between Groups Within groups Total	5.183 34.904 40.087	6 28 34	.864 1.247	.693	.657

There were no significant differences (p<0.05) in soil P concentrations between baseline (B) samples taken in March 2004 and post-treatment intensive (I) samples taken in September 2004 for any of the treatment rates of either Duofos or TSP under the intensive or sustainable nitrogen regimes (Figure 3. 8).

**Morgans soil P (mg/l) - Baselin v Intensive Nitrogen regimes**

Figure 3. 8.　Mean Morgan's soil phosphorus of samples taken from intensive Nitrogen regimes grass plots in September 2004.

Standard error confidence limits: p < 0.05 with five replicates.

One-way analyses of variance show no differences between treatments in either regime.

Table 3. 8 Analysis of variance results for Duofos vs TSP, under an intensive nitrogen regime. The dependent variable is difference (baseline – treated) in Morgan's soil P concentration.

		Sum of Squares	df	Mean square	F	Sig.
Duofos vs TSP	Between Groups	1.350	6	.225	.136	.990
	Within groups	46.432	28	1.658		
	Total	47.782	34			

There were no significant differences (p<0.05) between Duofos and TSP at any of the treatment rates in soil P concentrations (Morgan's soil P) from soil samples taken in September 2004 under the sustainable or intensive nitrogen regimes (Figure 3. 9).

Morgan's Soil P (mg/l P) - Sustainable and Intensive Nitrogen regimes
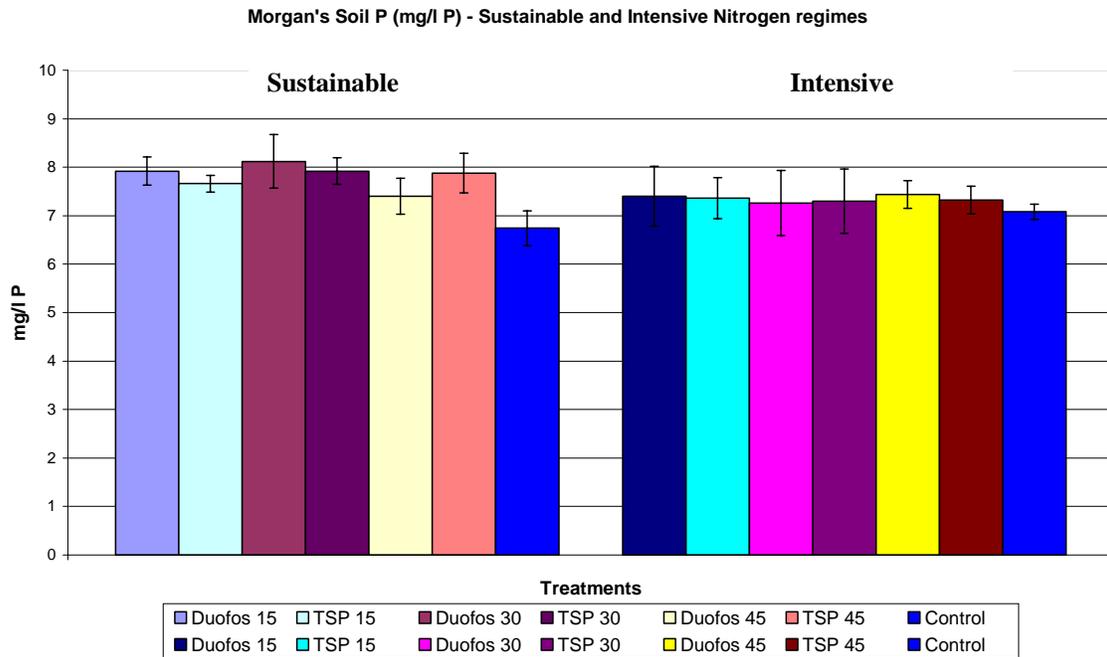

Figure 3. 9. Mean Morgan's soil phosphorus of samples taken from sustainable and intensive Nitrogen regimes in September 2004.

Standard error confidence limits: $p < 0.05$ with five replicates.

One-way analysis of variance show no differences between treatments in either regime.

Table 3. 9 **Analysis of variance results for sustainable vs intensive. The dependent variable is difference (Duofos – TSP) in Morgan's soil P concentration.**

		Sum of Squares	df	Mean square	F	Sig.
Intensive vs sustainable	Between Groups	5.183	6	.864	.693	.657
	Within groups	34.904	28	1.247		
	Total	40.087	34			

57

The soil pH of samples taken to 10 cm depth in September 2004 did not indicate any significant differences (p<0.05) between Duofos and TSP at any of the treatment rates (Figure 3. 10).

Soil pH - Intensive and Sustainable Nitrogen regimes
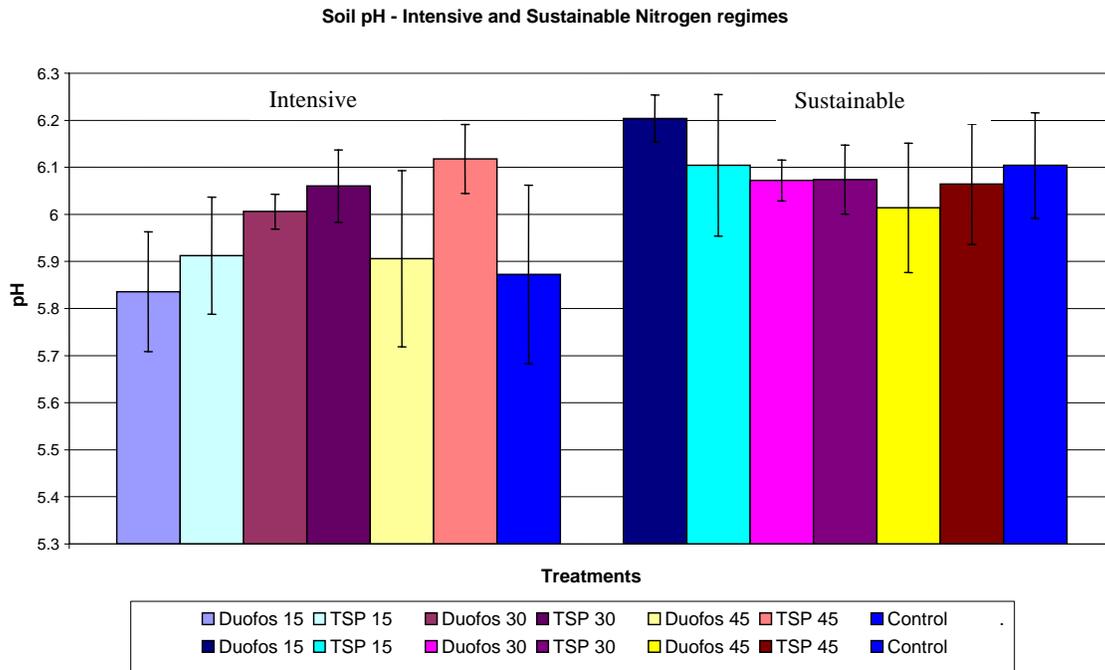
Figure 3. 10. Mean soil pH of samples taken from 10 cm depth from intensive and sustainable Nitrogen regimes in September 2004.

Standard error confidence limits: p < 0.05 with five replicates.

One-way analysis of variance show no differences between treatments in either regime.

Table 3. 10. Analysis of variance results forDuofos vs TSP. The dependant variable is soil pH. Results are presented separately for intensive and sustainable nitrogen regimes.

		Sum of Squares	df	Mean square	F	Sig.
Duofos vs TSP (intensive)	Between Groups Within groups Total	.327 2.129 2.456	6 28 34	.055 .076	.717	.639
Duofos vs TSP (sustainable)	Between Groups Within groups Total	.102 1.602 1.704	6 28 34	.017 .057	.297	.933

The soil pH of samples taken to 5mm depth in September 2004 did not indicate any significant differences (p<0.05) between Duofos and TSP at any of the treatment rates (Figure 3. 11).

pH of 5mm samples from Intensive Nitrogen regimes
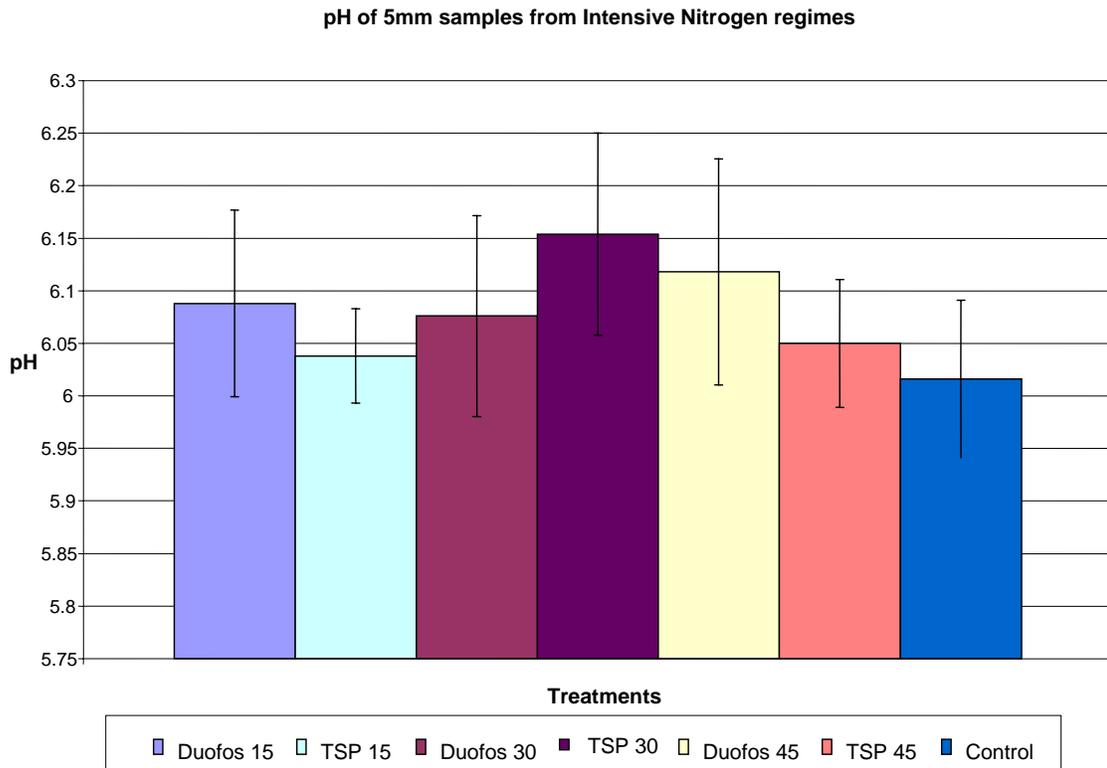
Figure 3. 11. **Mean soil pH of samples taken from 5 mm from intensive Nitrogen regimes in**

September

2004.

Standard error confidence limits: p < 0.05 with five replicates.

One-way analysis of variance show no differences between treatments

Table 3. 11. **Analysis of variance results forDuofos vs TSP. The dependant variable is soil pH at 5mm. Result is for intensive nitrogen regime.**

		Sum of Squares	df	Mean square	F	Sig.
Duofos vs TSP	Between Groups Within groups Total	.069 .984 1.053	6 28 34	.011 .035	.325	.918

Discussion

There were no significant differences in dry matter (DM) yield between Duofos and TSP under any of the treatment rates, or compared with controls, in either the intensive or the sustainable nitrogen regimes (Figure 3. 4, Figure 3. 5). A number of sites were investigated before setting up the yield trials but all sites had P applied within the previous six months and were P index 3 (6 – 10 mg/l soil P) or higher, demonstrating the over-accumulation of P in Irish farm soils. Murphy and Culleton (2000) recommended that index 3 P is required for intensive agriculture and they found that no significant increase in beef yield was achieved by increasing the P application rate from 15 to 30 kg/ha P based on a trial conducted over thirty years where the soil P was 6 mg/l P (index 3) at the start of the trial (Culleton, N. personal communication). Carton et al. (2005) published results from five sites in Ireland where a positive yield response to P applied to wheat grown on soils at P index 1 was achieved but these exceptionally low P sites would be very uncommon on commercial farms.

Plant leaf samples analyzed for P concentrations did not reveal any significant differences between Duofos or TSP treatments, or compared with controls ($p<0.05$) (Figure 3. 6). Luxury P uptake by plants does not occur to any great extent (Sharply *et al*, 1994b). Ozanne (1980) reported that total P taken up by plants is related to yield rather than concentration in the tissue and concluded that the major factor determining P uptake appeared to be the demand of the above ground vegetation or its ability to dilute absorbed P.

There were no significant differences ($p<0.05$) between Duofos and TSP at any of the treatment rates in soil P concentrations (Figure 3. 9) from soil samples taken in September 2004. Similarly, there were no significant differences in soil P concentrations between baseline samples taken in March 2004 and post-P treatment samples taken in September 2004 for any of the treatment rates of either Duofos or TSP (Figure 3. 7, Figure 3. 8). Where soil-P concentrations are already high the rate of uptake of P does not increase proportionally but approaches a maximum (Asher and Lonergan, 1967). This is the most likely reason for the lack of yield response to any of the treatments under, for

example, the intensive nitrogen regime (250 kg/ha N) where the grass production levels were relatively high at 1942 kg/ha even in the untreated P control plots for the second harvest (Figure 3. 4).

The standard practice for sampling of agricultural soils in Ireland is to a depth of 10 cm (Teagasc 2004). The mean soil pH of samples taken at the trial site in September 2004 did not indicate any significant differences between Duofos and TSP at any rates (Figure 3. 10; Table 3. 10). Mulqueen et al (2004) favoured sampling at 20mm depth because their research showed that the main release of P takes place from the top 20mm of soil. Murphy and Culleton (2000) observed larger concentrations of P nearer the surface in samples taken at 5 mm depth compared with samples taken at 10 cm. Soil samples taken at the trial site at depths of 10 cm and 5 mm in September 2004 did not indicate any differences in pH following Duofos and TSP treatment (Figure 3. 10; 3. 11). The relatively low concentrations of calcium in Duofos (100 g/kg) and TSP (194 g/kg) (Table 1. 1), would not be expected to have a significant effect on soil pH beyond the immediate granule zone.

A survey of Irish farm soils carried out by Culleton et al (1996) concluded that some 20% of the soils analysed for nutrient status had P levels in excess of soil P index 4 (>10 mg/l P) (Morgan's P soil test). The initial soil P concentrations in this trial were relatively high at 7.24 mg/l P prior to the trial in March 2004. These high baseline concentrations of P are the most likely reasons for the lack of response in yield, plant tissue and soil P to all rates of Duofos and TSP. There is currently a strong trend toward reducing the phosphorus recommendations for crop production (Teagasc, 2004) and there is evidence that optimum livestock production can be achieved at soil P index 2 (3-6 mg/l P) (Murphy and Culleton, 2000). Additional research is required to investigate these factors and a trial site with a lower P index (e.g. P index 2).

Chapter 4

General Discussion

Efforts are being made within industry and agriculture to reduce and where possible to recycle waste with high phosphate content. Despite this only modest impacts have been made upon the large amounts of phosphate transported in rivers and estuaries. While domestic, municipal and industry sources are contributors to phosphate pollution in waterways; agriculture in the more advanced countries is a continuing source of phosphorus pollution. Unlike municipal and industrial sources agriculture tends to occur as non point sources over wider areas. The application of organic and inorganic P fertilizer in relation to rainfall events and soil water conditions have a considerable influence on P transfer through overland flow (Haygarth and Jarvis, 1997).

The national soil P index which was at P index 1 (0-3 mg/l P) in 1951 (Walsh et al., 1957) now averages index 3 (8.1mg/l P) in 2002 (Herlihy and McCarthy 2004) following almost fifty years of high farmland P application. Culleton et al. (1996) concluded from a comprehensive nationwide survey of Irish soils that 20% had P levels in excess of 10 mg/l and that these concentrations were unnecessary for optimum production. This dramatic increase in P concentrations in Irish soils has given positive benefits to crop yields but has resulted in excess P inputs to aquatic systems. The dry matter yield results from this research (Figure 3. 4, and Figure 3. 5) demonstrate that with varying P application rates (Table 3. 2) dry matter yield may not be significantly influenced over a control receiving no P application at soil P index 3 or greater.

In this trial there was significantly less overland flow of DRP (Figure 2. 7), acid hydrolyzable P (Figure 2. 8) and total P (Figure 2. 9) in the case of Duofos compared with TSP on the majority of simulated rainfall/collection dates. The lower overland loss of P from Duofos may be partly due to the higher organic matter content of the granule (86 g/kg) compared with TSP (5.6 g/kg) (Table 1. 1) that increases the sorption capacity of the granule thus slowing the release of P. The relatively high concentration of Al and Fe (Table 1. 1) in Duofos is also expected to have had a significant effect on the solubility of P in the formulation. These combined effects may explain the slow release characteristics of Duofos compared with TSP.

Possibly the most beneficial advantage demonstrated by Duofos was recorded on July 15-16th following 48 hours of rainfall (Figure 2. 6). The eighteen days following the P treatments on June 27th were marked by a long dry spell. Then on July 14th there was a period of rain that lasted for 48 hours at the trial site. This rain just preceded and coincided with the rainfall simulation/collection on July 15-16[th.] Significantly higher concentrations of DRP, acid-hydrolyzable P and total P were recorded in the case of TSP (Figure 2. 7, Figure 2. 8, Figure 2. 9).

This sudden peak of P release on the soil surface could potentially pose a high risk of pulse or flash pollution of phosphorus to waterways. The lower concentrations of P collected from the Duofos treated plots indicate a much lower mobilization of P during and after heavy rainfall. This is potentially a key environmental advantage for Duofos over TSP especially in the relatively high rainfall Irish climate.

There is an urgent need to re-consider how to manage P inputs efficiently for a profitable agricultural industry, yet maintain a diverse range of aquatic and terrestrial ecosystems, with due regard to the efficient exploitation of natural P reserves (Sharpley et al., 2005). This requires a more proactive implementation of cost effective and targeted Best Management Practices (BMP) with mutual farmer-regulator agreement of local solutions to local problems (Sharpley et al., 2005). Not alone should the amount of P fertilizer applied be considered but also the persistence (seasonal) (Figure 2. 7, Figure 2. 10) stability (in extreme rainfall events) (Figure 2. 7) and availability (for plant uptake) to achieve maximum efficiency and minimal detrimental environmental impact need to be taken into account. Schroder et al. (2003) suggested a global harmonisation of environmental policy approaches to nutrient losses, including regulation, based on various criteria to ensure it is effective. This would allow land managers (farmers, foresters, recreational land managers) the greatest freedom to apply best management practices and select only those measures they consider effective under their specific circumstances.

Environmental pollution from elevated nutrient concentrations (including P) in overland flow has gained attention at EU level and the introduction of regulation with the publication of 'The Nitrates Directive' (1991) followed on by the 'Code of Good Farming Practice' (2005) is an indication of the willingness at European level to legislate and resolve the impact of excessive nutrients in surface waters leading to water pollution. However, enforcement of the Nitrates directive is only now (2006/2007) being imposed at farm level with fines and deductions from 'Single Payment Schemes' for offenders found in non-compliance with these directives.

The Rural Environmental Protection Scheme (REPS) introduced the concept of organic farm waste trading between farms with particular emphasis on slurry and farmyard manure imports to tillage farms from livestock farms with high P index soils. Participation in REPS 3 was closed to new applicants on October 2006 and a replacement REPS 4 will commence in 2007. The main emphasis in REPS to date was farm waste/nutrient management with organic and chemical P applied only on the basis of soil sampling and analysis and soil P index. An opportunity now exists to further develop the concept of lower environmental risk fertilizer usage by introducing Duofos, particularly in P risk zones, sloped areas near water bodies and high rainfall areas could be achieved via REPS 4 with recommendations included under the scheme.

There is scope for a reduction of potential P loss from soil by careful land management and an approach toward optimum use of phosphate fertilizer, particularly with the use of an organic granule formulation such as Duofos as demonstrated in this research.

From this research a number of recommendations can be made:

- o Duofos can be recommended over Triple Superphosphate to reduce P overland flow especially on gently sloped grassland pastures (Chapter 2).

o Recommendations for use of Duofos in sensitive locations should be included under the new REPS 4 scheme to reduce the risk of high P loss from pastures.

o Duofos can have a particularly important environmental advantage over TSP in the period immediately following rainfall or during high rainfall periods (Figures 2. 7; 2. 8; 2. 9).

o At P soil index 3 or higher no yield increase can be expected from the application of additional P either in the Duofos or the TSP formulations at intensive (250 kg/ha) or sustainable (25 kg/ha) concentrations of nitrogen (Chapter 3).

Chapter 5

References

Allen, S.E., 1989. *Chemical Analysis of Ecological Materials*, Blackwell Scientific Publications, Oxford, pp15-16.

Anuradha, M. and Narayanan, A., 1991. Promotion of root elongation by phosphorus deficiency. *Plant soil,* **136**, 273-275.

Asher, C.J. and Lonergan, J.F., 1967. Response of plants to phosphate concentration in solution culture. I. Growth and phosphorus content. *Soil Sci.* **103**: 225-233.

Barrow, N.J., Boden, J.W., Posner, A.M., Quirke, J.P., 1980. An objective method of fitting models of ion adsorption on variable charge surfaces. *Australian Journal of Soil Research,* **18**, 37-47.

Barry, D. A. J. and Miller, M. H., 1989. Phosphorus nutrition requirement of maize seedlings for maximum yield. *Agron. J.* **81**, 95-99.

Bould, C. and Parfitt, I.R., 1973. Leaf analysis as a guide to the nutrition of fruit crops. In: Magnesium and phosphorus sand culture experiments with apple. *J. Sci. Food Agric.* **24**, 175-185.

Bowyer-Bower, T.A.S. and Burt, T.P. 1989. Rainfall simulators for investigating soil response to rainfall. *Soil Technology*. **2**, 1-16.

Brady, N.C., 1990. *The Nature and Properties of Soils*, 10th edn. Macmillan Publishing Company, New York, 621 pp.

Carton, O.T., Coulter, B.S., Herlihy, M. and Hackett, R.A., 2005. Nutrient applications to Tillage Crops and Their Environmental Implications. In: *Proceedings of Agricultural Research Forum, Tullamore.* 2002.

Chambers, B.J., Garwood, T.D.W., and Unwin, R.J., 2000. Controlling soil water erosion and phosphorus losses from arable land in England and Wales. *Journal of Environmental Quality* **29**: 145-150.

Culleton, N., and Murphy. J., 1996. The evaluation of environmental, agronomic and economic implications of high and low input dairy systems. *Teagasc Research Report 1996.* In Johnstown Castle Research Centre, Wexford pp 3-4.

Culleton, N., 2007. Teagasc, Johnstown Castle Research Centre, Co. Wexford. Personal communication.

Daly, K., Mills, P., Coulter, B. and Martin, M., 2002. Modeling Phosphorus Concentrations in Irish Rivers Using Land Use, Soil Type, and Soil Phosphorus Data. *J. Environ.Qual.* **31**:590-599.

Daly, K and Styles, P., 2005. *Phosphorus chemistry of Mineral and Peat Soils in Ireland.* EPA, Ardcavan, Wexford. www.epa.ie

Daniel, T.C., Sharpley, A.N., Lemunyon, J.L., 1998. Agricultural phosphorus and eutrophication: a symposium overview. *J. Environ. Qual.* **27**, 251-257.

Delta-T Devices. HH2 Moisture Meter user manual version: 2; Delta & Co, UK.

Dils, R.M. and Heathwaite, A.L., 1996. Phosphorus fractions in hillslope hydrological pathways contributing to agricultural runoff. In: Anderson, M.G., Brooks, S.M., (Eds.), *Advances in Hillslope Processes*. Wiley, Chicester, pp. 229-251.

Fowler, J. and Cohen, L. 1990. *Practical Statistics for Field Biology*. John Wiley and Sons Chichester.

Foyer, C and Spenser, C., 1986. The relationship between phosphate status and photosynthesis in leaves. Effects of intracellular orthophosphate distribution, photosynthesis and assimilate partitioning. *Planta* **167**, 369-375.

Frank Wright Ltd., Blenheim House, Blenheim Road, Ashbourne, Derbyshire DE6 1HA.

Freeden, A.L., Rao I.M., and Terry, N., 1989. Influence of phosphorus nutrition on growth and carbon partitioning in Glycine max. *Plant Physiol.* **89**, 225-230.

Gibson, C.E., 1997. The dynamics of phosphorus in freshwater and marine environments. In: Tunney, H., Carton, O.T., Brookes, P.C., Johnson, A.E. (Eds.), *Phosphorus loss from soil to water.* CAB International, Guilford, UK, pp. 119-135.

Hach Company, 1998. *Hach Water Analysis Handbook*, 3rd edition, Colorado, USA, pp 525-545. PO.

Haygarth, P.M. and Jarvis, S.C., 1997. Soil derived phosphorus in surface runoff from grazed grassland lysimeters. *Water research* **31**: 140-148.

Herlihy, M. and McCarthy, J., 2004. Temporal Trends in Soil-Test P and P recovery in Grassland Soils. www.fertilizer –assoc.ie/publications

Huffman, E.O. and Taylor, 1963. The behaviour of water-soluble phosphate fertilizer in soil. J. *Agric. Food Chem*. **11**: 182-187.

Jordan, P., Menary, W., Daly, K., Kiely, G. Morgan, G., Byrne, P., Moles, R., 2004. Patterns and processes of phosphorus transfer from Irish grassland soils to rivers-integration of laboratory and catchment studies. *Journal of Hydrology* **304** 20-34.

Khasawneh, F.E., Sample, E.C., Hashimoto, I., 1974. Reactions of ammonium ortho- and polyphosphate fertilizers in soils: 1. Mobility of phosphorus. *Soil Sci. Soc. Am. Proc.* **38**: 446-451.

Khamis, S., Chaillou, S. and Lamaze, T., 1990a. CO2 assimilationand partitioning ofcarbon in maize plants deprived of orthophosphate. *J. Exp. Bot.* **41**, 1619-1625.

Kurz, I., 2002. *Phosphorus exports from agricultural grassland in overland flow and subsurface drainage water*. PhD Thesis. Department of Geology, Trinity College, Dublin. 200 pp

Kurz, I., Coxon, C.E., Tunney, H., Ryan, D., 2005. Effects of grassland management practices and environmental conditions on nutrient concentrations in overland flow. *Journal of Hydrology*. **304** (2005) 35-50.

Larsen, S., Gunray, D., and Sutton, C.D., 1965. The rate of immobilisation of applied phosphate in relation to soil properties. *Journal of Soil Science* **16**: 141-148.

Lawton, K. and Vomocil, J.A., 1954. The dissolution and migration of phosphorus from granular superphosphate in some Michigan soils. *Soil Sci. Soc. Am. Proc.* **18**: 26-32.

Lauer, M. J., Blevins, D. G. and Sierzputowska-Gracz, H., 1989b. P-nuclear magnetic resonance determination of phosphate compartmentationin leaves of reproductive soyabeans (Glycyne max L) as affected by phosphate nutrition. *Plant Physiol.* **89** 1331-1336.

Lindsay, W.L. and Moreno, E.C., 1960. Phosphate phase equilibria in soils. *Soil Sci. Soc. Am. Proc.* **24**: 177-182.

Lynch, J.M. and Whipps, J.M., 1990. Substrate flow in the rhizosphere. *Plant Soil* **129**, 1-10.

Marschner, H. 2003. *Mineral Nutrition of Higher Plants*. Academic Press. Elsevier Science. pp 889

McDowell, R.W. and Sharpley, A.N., 2002. Phosphorus solubility and release kinetics as a function of soil test P concentration. *Geoderma* **112** 143-154.

McGechan, M.B. and Lewis, D.R., 2002. Sorption of Phosphorus by soil, Part 1: Principles, Equations and Models. *Biosystems Engineering* **82** (1), 1-24.

Moreno, E.C., Lindsay, W.L., and Osborn, G., 1960c. Reactions of dicalcium phosphate dehydrate in soils. *Soil Sci.* **90**: 58-68.

Moore, P.A. and Miller, D.M., 1993. Decreasing Phisphorus Solubility in Poultry Litter with Aluminium, Calcium and Iron Amendments. J. *Environ. Qual*. **23**: 325-330.

Morgan, M.F., 1941. Chemical Soil Diagnosis by the Universal Soil Testing System. *Bulletin/Connecticut Agricultural Experimental Station 450*: pp 579-628.

Mulqueen, J., Rodgers M., and Scally, P., 2004. Phosphorus transfer from soil to surface waters. *Agricultural water management*. Elsevier

Murphy, W.E. and Culleton, N., 2000. *Teagasc, Johnstown Castle Report 2000.* Thirty years of Phosphorus fertilizer on Irish Pastures.

Nash, D., Hannah, M., Halliwell D., and Murdoch, C., 2000. Factors affecting phosphorus export from a pasture-based grazing system. *J. Environ. Qual*. **29**:1160-1166.

NRC. 2001. *Nutrient requirements for Dairy Cattle. (7th ed.).* National Academic Press, Washington, DC.

Ozanne, P.G., 1980. Phosphate Nutrition of Plants – A General Treatise. In: *The Role of Phosphorus in Agriculture*. Ed. American Society of Agronomy. pp 568-573.

Pinevich, V.V., 1959. In: *Soviet Soil Course*: No. 9. pp 1-118.

Peech, M. and English, L. 1944. Rapid micro chemical soil tests. *Soil Science*, **57**: 167.

P.T. Madura Guano, Desa Kebun, Kec. Kamal, Madura, Indonesia.

Radin, W. J., 1990. Responses of transpiration and hydraulic conductance to root temperature in nitrogen- and phosphorus deficient cotton seedlings. *Plant Physiol*. **92**. 855-857.

Rao, I. M. and Terry, N., 1989. Leaf phosphate status, photosynthesis and carbon partitioning in sugar beet. I. Changes in growth, gas exchange and Calvin cycle enzymes. *Plant Physiol*. **90**, 814-819.

Rossitter, R.C., 1978. Phosphorus deficiency and flowering in subterranean clover (Tr. subterraneum L.). *Ann. Bot*. (London) **42**, 325-329.

Sample, E.C., Soper, R.J., and Racz, G.J., 1980. Reactions of P Fertilizers in Soils. In: *Role of Phosphorus in Agriculture*. Am. Soc. Agron.

Schroder, J.J., Aarts, H.F.M. Ten Berge, H.F.M., Van Keulen, H., Neeteson. J.J., 2003. An evaluation of whole-farm nitrogenbalances and related indices for efficient nitrogen use. *Eur. J. Agron*. **20** (1-2), 33-34.

Schulte, R.P.O. and Herlihy, M., 2006. Quantifying responses to phosphorus in Irish grasslands: Interactions of soil and fertilizer with yield and P concentration. *Eur. J. Agron.* **26**, pp. 144-153

Sharpley, A.N., Abuja, L.R., Yamamoto, L.R. Menzel, R.G., 1981b. The kinetics of phosphorus desorption from soil. *Soil Sci. Soc. of Am. J.* **45**, 493-496.

Sharpley, A.N., Curtin, D., Syers, J.K., 1988. Changes in water extractability of soil inorganic phosphate by sodium saturation. *Soil Sci. Soc. Am. J.* **52**, 637-640.

Sharpley, A.N., Chapra, S.C., Wedepohl, R., Sims, J.T., Daniel, T.C. and Reddy, K.R. 1994b. Managing agricultural phosphorus for protection of surface waters: issues and options. *J. Env. Qual*. **23**, 437-451.

Sharpley, A.N., Withers, P.J.A., Abdalla C.W., and Dodd, A.R., 2005. Strategies for the Sustainable Management of Phosphorus. Soil Sci. Soc. Am. 677 S. Segoe Rd., Madison, WI 53711, USA. Phosphorus: *Agriculture and the Environment*, Agronomy Monograph No. 46.

Teagasc. Agricultural and Food Development Authority. *Nutrient and Trace Element Advice for Grassland, Tillage, Vegetable and Fruit Crops*. 2nd Edition 2004.

Treeby, M. T., Van Steveninck, R. F.M. and de Vries, H. M. 1987. Quantitative estimates of phosphorus concentrations within Lupinus luteus leaflets by means of electron probe X-ray microanalysis. *Plant Physiol*. **85**, 331-334.

Tunney, H., Breeuwsma, A., Withers, P.J.A., and Ehlert, P.A.I. Phosphorus Fertilizer Strategies: Present & Future. In: *Phosphorus Loss from Soil to Water* eds. Tunney, H., Carton, O.T., Brookes, P.C. and Johnston, A.E. CAB international 1997.

Tunney, H., Coulter, B., Daly, K., Kurz, I., Coxon, C., Jeffrey, D., Mills, P., Kiely, G., and G.Morgan, G., 2000*. Quantification of phosphorus loss from soil to water. Final report and literature review*. EPA*,* Wexford. www.epa.ie

van Doesburg, J.D.J., 1996. Particle size analysis and mineralogical analysis. In: *Manual for Soil and Water Analysis*. Backhuys Publishers Leidenn, Nl. pp 258-267

Wallbrink, P.J., Martin, C.E., Wilson, C.J., 2003. Quantifying the contributions of sediment, sediment-P and fertilizer-P from forested, cultivated and pasture areas at the landuse and catchment scale using fallout radionuclides and geochemistry. *Soil & Tillage Research* **69** 53-68.

Walsh, T., Ryan, P.F., and Kilroy, J., 1957. A half-century of fertiliser and lime use in Ireland. *Journal of the Society of Statistical and Social Inquiry, Ireland*. **19**: 104-136.

Wild, A. 1950. The retention of phosphate by soil. A review. *J. Soil Sci.* **1**:221-238.