THE USE OF ORGANIC AMENDMENTS IN THE RECLAMATION OF ACIDIC COAL MINE WASTE.

By

Thomas Alexander Bruce Walker B.Sc.

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Agricultural Chemistry Section
Department of Chemistry
University of Glasgow

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SUMMARY

The introductory chapter presents a review of the chemical, physical and biological properties of colliery spoil, and the problems which they represent to reclamation and revegetation. The general approaches already cited in the literature for overcoming such problems are looked at as well as the varying managerial practices and after uses that are often employed.

This is followed by a brief description of the field trials at Baads, Riddochhill and Loganlea and includes the rationale behind the choice of organic amendments, their suitability and supply. A number of problems resulting in poor establishment in the latter two trials are also discussed.

The build-up of organic matter in the spoil is of great importance to successful reclamation as it improves the physical structure of the material and is the major source of long-term nutrient supply to any established vegetation. Chapter 3 considers the use of the most common chemical methods for the determination of organic matter and organic carbon and shows them to be unsuitable because of the high level of background carbon in the unburnt shale preventing the unambiguous measurement of the build-up of carbon from plant and microbial sources. More successful was the measurement of carbon turnover, estimated by carbon dioxide evolution. This gave comparative figures for "biological activity" and carbon turnover in spoils which received different treatments.

Although the carbon turnover in the treated spoils was similar, there was considerable litter accumulation at the spoil surface which varied greatly between amendments. All the spoils showed a high level of carbon turnover, especially when compared to nitrogen and phosphorus.

Chapter 4 deals with the levels, distribution and turnover of the macronutrients nitrogen, phosphorus and potassium. Nitrogen and phosphorus are particularly important as they are usually deficient in colliery spoil. Measurements of nitrogen, phosphorus and potassium in the herbage, litter and spoil were made to determine how much of a nutrient capital had been accumulated in the system, and where it was located. The ability of the spoil to supply nutrients was assessed by mineralisation experiments. Information was also obtained on nitrogen cycling by measurement of nitrification. The results of these experiments confirmed that the colliery spoil was deficient in nitrogen and phosphorus, with the exception of the chicken manure treated spoil which contained appreciable amounts of available phosphate, and that little of these nutrients was being supplied. A small fertiliser response trial was set up which showed that vegetation established on reclaimed colliery spoil responded rapidly to the supply of nitrogen, but not phosphate and potassium.

A brief, concluding chapter discusses management practices in the light of the experimental results described previously.

CHAPTER 1

GENERAL INTRODUCTION TO COLLIERY SPOIL RECLAMATION

1.1 BACKGROUND TO RECLAMATION

The mining of underground mineral deposits such as coal, metal ores, sand, gravel, clay, limestone etc. can lead to the disruption of land surfaces where the native vegetation and animal communities have been removed and most of the topsoil is lost, altered or buried. The natural process of re-establishment is either very slow, or in some cases totally absent, due to the nature of the material brought to the surface. The natural processes of vegetation, succession and soil development can be artificially accelerated and this is generally termed as reclamation. Of all the waste materials brought to the surface during mineral excavations, that produced by coal mining can prove to be one of the most difficult to reclaim because of its inherently poor physical and chemical composition.

The earliest reclamation schemes were carried out by colliery owners or landowners where trees were planted directly on the spoil tips without any initial regrading. Many of these schemes failed, but on tips with low toxicity problems a mature vegetative cover eveloped with the tips being well integrated into the landscape. Early research into the problem of reclamation was dominated by foresters with the county authorities being assisted by

Forestry Commission grants to establish reclamation schemes (Doubleday 1974). However a condition of receiving a grant was that the schemes had to be directed towards commercial timber production which led to uniform and uninteresting stands. As a result of many of these schemes failing, and the increasing size of the spoil tips which could no longer be hidden by a screen of trees, it was concluded that the heaps had to be lowered by regrading. The pioneering work in this area was led by U. Aylmer Coates in the mid 1950's working in Lancashire. His work led to a new era in spoil tip reclamation.

By the mid 1960's the idea of reclamation had spread to other counties where the problem existed and since then derelict land reclamation has proceeded at an ever increasing pace. The continuing stimulus for reclamation has been in the form of grant aid from Central Government which was initiated in 1959 by the revival of the Industries Act (1945). The level of grant can vary from 50% to over 90% in certain circumstances. The majority of the work is carried out by local authorities who may have their own reclamation teams with staff qualified in engineering, surveying, valuation, landscape architecture, soil science, forestry and agriculture.

The Government policy towards derelict land reclamation has a number of interrelated aims (Broughton 1985):

1) Stimulating economic development either by providing new sites on reclaimed land for industry, commerce and housing, or by improving the local environment to

attract potential new employment.

2) Enhancing the quality of life for the local population who live in close proximity to the existing dereliction by converting the spoil tips into a modern development or pleasant areas of green open space.

3) The conservation of agricultural land by the use of reclaimed derelict land for industry, housing etc. which would otherwise have encroached on the greenbelt areas which often include high quality agricultural land.

There are in general six classes of land use that can be achieved after mineral excavation, and the ensuing reclamation scheme should be designed with at least one if not a combination of these in mind;

a) multiple uses with few chemical or physical limitations.
b) rural, urban, recreational or industrial building sites and grounds.
c) extensive recreational uses.
d) forestry production.
e) pasture, hay or speciality crops not requiring ploughing.
f) intensive agriculture including ploughing.

The choice of intended land use is governed to a great extent by the physical and chemical nature of the waste material concerned and also the availability of ameliorants that would be required to reclaim the land to its preferred use.

The desired goal since the mid 1960's has been to maximise the numbers of reclaimed sites to be developed for industrial, commercial and residential uses. The advantages being a boost in economic development, a conservation of land resources, and at the same time the after-sale value of the land offsetting the reclamation costs. This is the ideal situation, but in reality the majority of reclaimed land up to the 1980's has been established for agriculture or public open spaces (Broughton 1985).

Thus the prime aim of most reclamation schemes is to initiate revegetation and create a satisfactory spoil cover. The revegetation provides rapid visual improvement, reduces air and water pollution, and stabilises surfaces enabling the material to be developed for a range of after uses.

It is the aim of this study to identify some of the major nutritional and chemical problems associated with colliery spoil reclamation, and to investigate the use of organic amendments as an aid to vegetation establishment and spoil development.

1.2 COAL MINING IN BRITAIN

Coal mining in Britain dates back to Roman times, if not earlier, and while the value of coal has long been established, it has only recently been learned how to control the industry so that it not only yields an essential fuel, but does so without destroying the environment (Doubleday 1974).

Coal can be extracted either by removing the overburden from shallow seams, open-cast mining, or by sinking a shaft to deeper seams and removing the coal, deep mining. The latter accounts for roughly 80% of coal production in Britain.

1.2.1 Opencast mining

Opencast mining involves the exposure of the coal seam by the removal of the overlying soil and rocks, with the subsequent extraction of the coal from above. This method of coal production was introduced to Britain in 1941 and the initial schemes were only deemed feasible when the overburden:seam thickness was less than 10:1. However since the mid 1960′s this ratio has been increasing due to the continuing improvement in mining technology.

There are distinct advantages in the use of surface mining compared to deep mining in that the excavation can be developed more rapidly, there are lower capital and labour costs per tonne of coal produced, it is less hazardous to the miners′ health and lives, and it recovers a higher proportion of the coal reserve. On the other hand the environmental impact of surface mining may be greater as it can involve the relocation of farms, diversion of streams and rivers, adjustment of water tables and removal of forests.

The restoration of land after opencast mining is presently governed in Britain by the Opencast Coal Act (1958). This places the responsibility for reclamation on the producer which represents approximately 5% of the total cost of mining operations (Arguile 1975). In the initial stages of mining the topsoil and subsoil are removed and stored separately. The overburden is then excavated and mining commences. In the final restoration the overburden is replaced in stratigraphic order, followed by subsoil and topsoil with the surfaces graded to give efficient drainage. Restoration should proceed as soon as possible after coal extraction to reduce any detrimental effects of storage in the soil properties. After restoration the operators retain the responsibiltiy of aftercare and maintenance for a minimum of five years.

1.2.2 Deep mining

Underground mining is more complex than surface mining involving the construction of tunnels and railways and the transportation of men and coal at depths often exceeding 1000 m. After the coal has been removed the tunnel roof may be supported in two ways, either by constructing supports behind the cutting machinery or by leaving pillars of coal behind as a natural support. There is an alternative form of deep mining which can remove a greater proportion of the coal seam, "longwall mining", and involves letting the tunnel collapse behind the cutter. However this may result in deformation of the overlying strata and subsidence of the land surface which has led to a great number of claims against the National Coal Board.

Deep coal mining results in the production of a large quantity of waste material consisting largely of shale, sandstone and other rock fragments. It has been estimated that for every five tonnes of coal extracted, one tonne of waste material is brought to the surface (Richardson 1976). At present day production levels, approximately 17.5 million tonnes of waste will be brought to the surface each year to add to that which has been produced in the past which Gutt et al. (1974) estimated at 3,000 million tonnes. There is an obvious problem therefore of how this vast quantity of material is to be disposed of.

In the extraction of coal only one sixth of the volume of material brought to the surface is waste, so there is ample space left in the worked out mine to accommodate it. However, although some stowage underground is carried out in West Germany, very little is done in Britain due to the vast expense this would entail to modify existing extraction machinery. A small proportion of the waste spoil is utilised for the backfilling of quarry workings, roadworks and other civil engineering activities because the physical nature of the material allows good compaction to give a firm base for construction. There has also been a great deal of research into the use of spoil as an aggregrate in brick production (Gutt et al. 1974; Lawson and Nixon 1978) and in concrete production (Bryenton and Rose 1976), but again this only accounts for a small proportion of the spoil material produced.

Therefore, as in the past when coal mine waste was dumped indiscriminately with little thought or planning as to the effects the material may have on the environment, the majority of the waste material produced in recent times is dumped either at sea or inland. It was estimated that in 1971/72, approximately 50 million tonnes of spoil were deposited on inland sites in Britain with a further 6 million tonnes dumped at sea. Of the land-dumped material only about 7 million tonnes were utilised, mainly for backfilling etc. (Gutt et al. 1974). A study by James (1982) suggested that existing tips in Britain owned by the National Coal Board contained 2,500 million tonnes of spoil and covered 11,000 hectares, with a further 500 million tonnes in private ownership.

In general these tips or "bings" are to be found on land adjacent to the mines where the material was dumped from a conveyer line forming a progressively higher cone with a long sloping tail up which the conveyer tracks ran. If material was being dumped from more than one mine then a series of peaks could develop, or in some cases a plateau was formed at the top. These bings may have risen to over 50 m in some cases, and were all characterised by steep, unstable slopes which tended to slip and dislodge any naturally establishing plants. These steep, unvegetated slopes when exposed to weathering are ideal surfaces for wind and water erosion resulting in a range of environmental problems.

1.3 COAL BINGS AND THE ENVIRONMENT

Although coal bings may cover only a limited area of land, a consequence of their severe physical and chemical nature is that they have an effect over a wide area of surrounding land.

1) In Britain it was common place for communities to develop in close proximity to the mine workings overshadowed by the spoil tips, often long after the mines were worked out. Many of the larger bings dominated the landscape for a considerable distance and therfore for aesthetic reasons alone reclamation is justified in order to blend them into the surrounding landscape. In Germany a system of progressive reclamation has been developed to minimise the visual impact of mining on the surrounding area. The waste is deposited in layers, moving in a stepwise formation with the resulting slopes being less severe than those developed under overhead tipping. As each layer is completed it is treated and planted with trees with the result that the lower slopes are screened from view while dumping continues (Doubleday 1974). In the United States and Canada the problem of aesthetics are minimal as mining and dumping are often carried out in remote areas where there is little pressure for reclamation and in general a low maintenance cover is suitable with the land being designated as a "wilderness" area.

2) The local communities and areas further afield may also be affected by noxious fumes released from some bings. No matter how efficient the extraction procedure, there will always be a certain amount of coal associated with the waste material and when this comes into contact with air trapped within the spoil then heat can be generated. If the exposure to air results in combustion, then gases such as carbon dioxide, carbon monoxide and nitrous oxide are emitted, and in the oxygen deficient conditions under which combustion within the tip occurs, then hydrogen sulphide and ammonia are released.

3a) If the pit heaps are left unprotected, then the subsequent weathering of the shale material results in a fine particulate material which can be carried for considerable distances by the wind. This leads to contamination of surrounding soil, streams and vegetation, the discolouration of nearby buildings, and may also aggravate human respiratory disorders.

b) Unprotected slopes are also susceptible to sheet and gully erosion which can carry large quantities of material into streams and rivers (Richardson 1976).

These problems may be greatly reduced by the establishment of a vegetation cover which protects the surface from the direct effect of the wind and stabilises the spoil with the roots binding the material together.

4) The oxidation of iron pyrites produces acid that can leach into surrounding streams lowering the pH and affecting aquatic life downstream of the bing. This lowering of pH may also mobilise certain trace metals that can affect water quality for a considerable distance downstream (Pulford et al. 1983). Blessing et al. (1975) observed similar stream pollution from abandoned mines in Australia, while Benza and Lyon (1975) estimated that 3,000 of the 50,000 miles of streams in Pennsylvania were polluted by acid mine drainage.

A certain degree of reclamation therefore is required to alleviate some of the aforementioned problems, and a prior knowledge of the nature of the material to be reclaimed would improve the chances of success of any reclamation scheme.

1.4 PHYSICAL PROBLEMS ASSOCIATED WITH COLLIERY SPOIL

The waste material found in colliery spoil heaps consists usually of shale, sandstone, mudstones and coal itself, with the shale being the dominant material which can often constitute over 90 per cent of all the waste. There can also be iron pyrite, calcium, magnesium and iron carbonate minerals present to a minor extent.

It is often the case that material from a range of different workings is brought together and dumped at a common heap. This can lead to a wide degree of heterogeneity within one tip. This problem is amplified if the tip contains washery waste which consists of small particles of coal, silt and clay that can hold up to 80 per cent moisture and when dry has a very poor structure. Shales originating from different areas may have a considerable range of weatherability and hence weathering products which will also affect the physical and chemical nature of the tip.

Weathering influences the particle size distribution of shales, with the breakdown of the larger particles being observed in the first few decades after tipping (Hall 1957, Richardson 1957,1958, Down 1974, 1975a). Richardson (1975) has demonstrated that the infiltration rate of freshly tipped material is high, but that on weathering the pore size in the surface layer becomes reduced until the stage where water infiltration is less than rainfall. On unreclaimed tips that generally have slopes of $32\text{-}36^{\circ}$ (Down 1975a) this runoff leads to erosion which will remove all the soil forming particles. This surface instability leads in turn to very poor vegetation establishment with the result that the spoils remain exposed to the action of wind and rain.

The majority of erosion problems can be solved by careful regrading and Downing (1971) recommends a theoretical slope of 1:40 to 1:50. In practice however, if vegetation can be established then slopes of 1:10 are possible. It is essential that the slopes are not too slight, and that low lying areas are avoided to prevent any problems of waterlogging.

The particle size distribution that results from the weathering of the shale material has a great influence on the spoil structure and texture that will develop and in turn influence bulk density, drainage and water holding capacities.

The spoil texture that evolves varies greatly depending on the nature of the waste material and its age. On poorly weathered material a coarse texture will develop that will have a low water holding capacity and will suffer through lack of moisture in dry weather. At the other extreme, the production of fine material leads to a reduction in the spoil porosity with the ensuing material becoming highly susceptible to waterlogging. Soils are heavily dependant on organic stabilising agents to maintain their structure and physical condition so that they remain favourable for root growth. The total absence of humified organic matter in colliery spoil means that the structure is likely to remain poor until some form of organic fraction is built up within the spoil. Rimmer (1982) showed an increase in organic matter with age in the top 5 cm of some reclaimed colliery heaps and similar results were also found by Down (1975b) and Schafer et al. (1980). However to improve spoil structure and hence water regimes in the rooting zone, organic matter must be incorporated to a greater depth.

The bulk density of spoil material tends to be higher than for natural undisturbed soils due mainly to the greater proportion of less weathered rock fragments (Smith et al. 1971). The bulk density of the spoil can be increased further during regrading as the poor structure cannot withstand the pressure caused by the earth-moving vehicles and can become severely compacted. These high bulk densities can impair water and air movement and greatly restrict root penetration resulting in poor plant establishment.

In unburnt colliery spoil, the predominantly black surface of the shales leads to problems of high surface temperatures. There can be as much as 10°C difference between adjacent south-facing soil and spoil slopes (Richardson 1976, Down and Stocks 1977, Jaynes et al. 1983) and surface temperatures in excess of 50°C have been recorded (Fitter and Bradshaw 1974). Such temperatures lead to immediate dieback of colonising species and also of newly grown roots of existing plants. Mulches can be used to reduce surface temperature thus aiding seedling development. Once a vegetation cover has been established the spoil tends to absorb less heat because of the heat dissipating abilities of the plants. This results in a cooler microclimate at the spoil surface which leads to an improvement in the germination rate (Schramm 1966).

1.5 CHEMICAL PROBLEMS ASSOCIATED WITH COLLIERY SPOIL

There are two main chemical problems associated with colliery spoil, the oxidation of pyrite which generates acidity, and the lack of essential nutrients in the spoil.

1.5.1 Pyrite oxidation

The most important chemical change that takes place in colliery spoil is the oxidation of pyrite, the others generally occur as a result of the acid production from this reaction (Chadwick 1973, Caruccio 1975, Pulford and Duncan 1975a, Costigan et al. 1981). The chemical oxidation of pyrite can be shown in a simple form by the following equations:

a. Oxidation by oxygen

$$2FeS_2 + 2H_2O + 7O_2 \text{ ---> } 2Fe^{2+} + 4H^+ + 4SO_4^{2-}$$

$$4Fe^{2+} + 10H_2O + O_2 \text{ ---> } 4Fe(OH)_3 + 8H^+$$

b. Oxidation by Fe^{3+}

$$FeS_2 + 14Fe^{3+} + 8H_2O \text{ ---> } 15Fe^{2+} + 2SO_4^{2-} + 16H^+$$

In certain circumstances bacterial oxidation of pyrite may also take place which will assist the chemical reactions. Reduced sulphur compounds are used as an energy source by <u>Thiobacillus</u> <u>thiooxidans</u>, and the oxidation of iron is carried out by <u>Thiobacillus ferrooxidans</u>.

There are in general six products that can result from the oxidation of pyrite; ferrous mono sulphide, ferrous sulphate, sulphuric acid, sulphur dioxide, hydrogen sulphide and free elemental sulphur.

Of these oxidation products, the sulphuric acid gives rise to the severest problems in terms of plant growth. Apart from the direct effect of the acidity on plant roots, there are also a number of secondary reactions that take place,

The very high hydrogen ion concentration leads to a dominance of the hydrogen ions on the cation exchange sites with a resultant reduction in base saturation and loss of the major bases which when in solution are readily leached from the rooting zone. The high levels of acidity may also result in the breakdown of the clay lattices which reduces the cation exchange capacity of the spoil and hence its ability to buffer against any further acid production. As the clay lattices break down, large quantities of aluminium are liberated into the soil solution and at the low pH values found in some spoils the aluminium and other trace metals such as manganese, iron, zinc and copper become soluble and available to plants leading to toxicity problems (Pulford et al. 1983).

High concentrations of soluble salts can be produced from both pyrite oxidation and acid breakdown of spoil minerals which can adversely affect vegetation by increasing the osmotic pressure of the soil solution (Donovan et al. 1976, Bradshaw and Chadwick 1980), and impairing the spoil physical condition via dispersion resulting from high sodium levels. Direct injury to plants may also result from imbalances or excesses in cation uptake. The acid conditions may reduce the availability of certain ions, and in particular phosphate, by producing oxide and hydroxide films of aluminium and iron which adsorb or complex phosphate so inducing deficiency (Pulford and Duncan 1975a, Costigan et al.

1982).

The temporal and spatial variation of toxicities in colliery shales has been reported by a number of authors (Palmer 1970; Doubleday 1970, 1971; Chadwick 1973, 1974; Fitter et al. 1974; Pulford and Duncan 1975b), particularly in relation to weathering. In general, when shales are first dumped, they have a fairly high pH (~7), but on weathering in the first five years this can drop rapidly to as low as 2.5. The shales then tend to remain acid for any period up to a hundred years or more until the reservoir of oxidisable pyrite is depleted, at which point the pH rises slowly to around a value of 5.

In general the temporal variation results in a bimodal distribution of pH values for samles taken from a large number of sites (Doubleday 1971, Kent 1979) where the larger peak at the lower pH range of 3-4 represents the actively weathering shales, and the smaller peak at the pH range of 6-7 represents either non-toxic shales, or those that have been recently tipped.

This problem of variation in pH values is enhanced by the problem of potential acidity, which is the amount of oxidisable pyrite left in the shale material. Parts of the same tip may be derived from coal seams with very different pyrite content with the result that the weathering characteristics of the spoil can change within a distance of less than a metre. In addition there appears to be two distinct types of pyrite, the massive form which has grains > 400 μm and tends to be unreactive, and framboidal pyrite which consists of clusters of spheres of about 25 µm in diameter, each sphere being made up of small crystals 0.25 µm in diameter. This form is readily oxidisable (Caruccio 1973).

This large degree of variation in acidity and its associated toxicities leads to tremendous difficulties in identifying problem areas requiring remedial action.

1.5.2 Nutrient Availability

Of the seventeen elements that are at present regarded as being essential for plant growth (Brady 1974), nine can be classed as macronutrients ie. required in relatively large amounts, and eight as micronutrients or trace elements.

1.5.2.1 Macronutrients (C, H, O, N, P, K, Ca, Mg, S)

Carbon, hydrogen and oxygen are obtained from atmospheric carbon dioxide and water, while the remaining six elements have to be made available in spoil solution to be utilised by plants.

a. Nitrogen.

To a large extent nitrogen availability governs the level of plant growth (Doubleday 1971), and is regarded as the element most restrictive to plant growth in colliery spoil (Williams 1975, Bloomfield 1982).

Nitrogen is usually supplied by the mineralisation of the organic matter fraction in natural soils. However since this fraction is negligible in unamended colliery spoil the nitrogen has to come almost entirely from the inorganic fraction. Pulford (1976) found total levels of nitrogen in the range of 1,000-8,000 mg N/kg which are similar to those reported by Chadwick (1981).

Although small amounts of this fossil nitrogen can be released on weathering (Cornwell and Stone 1968) especially under acid conditions, the levels are usually too low to encourage any plant establishment.

b. Phosphorus

Colliery spoil contains very little available phosphate, and as the shale becomes more acid, phosphate availability is reduced. At low pH´s the phosphate can be precipitated by forming a complex with soluble iron and aluminium. These colloidal precipitates slowly become more crystalline which decreases the phosphate availability.

Phosphate can also be adsorbed on to charged surfaces of iron and aluminium oxides and hydroxides that form as coatings on the spoil mineral particles. The phosphate ions may also enter into isomorphous exchange with silicate and hydroxyl ions of crystal lattices. Both of the latter processes can also render unavailable any phosphate that is applied as a fertiliser.

c. Potassium

Of the three major macronutrients, potassium presents the least problem. In general it occurs in abundance in the lattices of the clay minerals (Kohnke 1950, Doubleday 1970, Gemmell 1973) and becomes available on weathering. Acidic conditions can reduce the availability of potassium, but this can be easily rectified by liming.

d. Calcium and magnesium

Calcium and magnesium are unlikely to be deficient in neutral or alkaline spoils, but may become so in acid material. As liming would probably be undertaken in these materials the problem is usually overcome.

e. Sulphur

The main source of sulphur in colliery spoil is pyrite which on weathering releases sulphate, which is the form of sulphur that is taken up by plants. Therefore in pyrite bearing spoil sulphur availability is not a problem. However non-pyritic spoil may suffer from sulphur deficiency.

1.5.2.2 Micronutrients (Fe, Mn, B, Mo, Cu, Zn, Cl, Co)

Trace element availability can have an effect on plants in two ways, the first being their direct effect on plant growth in which they promote growth at low levels but can be toxic at high concentrations, the second by affecting the uptake of other nutrients required by the plant (Russell 1973).

In colliery spoil the levels of trace elements may be a limiting factor to plant growth. However unlike the macronutrients the problems encountered are those of toxicity rather than deficiency but in relation to the other toxicity problems their effect is usually negligible (Tasker and Chadwick 1978).

1.6 THE BIOLOGICAL STATUS OF COLLIERY SPOIL

It has been reported that unamended colliery spoil material can be characterised by its near total lack of organic matter and its very limited support of biological activity (Reeder and Berg 1977, Fyles et al. 1985). In a young developing soil, organic matter and associated humus are essential for improving and maintaining the soil structure and hence moisture levels in the rooting zone. It is also a source of major nutrients from mineralisation by micro-organisms releaseing inorganic ions into the soil solution.

Without the addition of organic matter and associated micro-organisms, colliery spoil will never develop into a well-structured medium that has the ability to cycle nutrients and hence sustain any vegetative growth. A complicating factor of the harsh physical conditions in the spoil is that certain soil fauna such as earthworms are not generally in evidence with the result of poor organic matter incorporation and the rapid build up of a surface mat that makes little contribution to the improvement of the spoil as a whole.

1.7 GENERAL SPOIL RECLAMATION TECHNIQUES

There are usually three basic aims behind any reclamation scheme:

i) To provide a topography that allows sufficient drainage to prevent waterlogging, but which also removes any opportunities for erosion to develop.

ii) To improve the spoil structure to promote plant growth.

iii) To modify any adverse chemical conditions in the spoil that may lead to acid leaching, nutrient deficiency or toxic levels of salt accumulation.

The normal sequence of operations required to achieve these aims are as follows:

Step 1) Regrading of the bing.

Step 2) A covering of soil can be used when available, otherwise the spoil is treated directly which usually entails cultivations and the application of lime.

Step 3) Nutrient application.

Step 4) Seeding.

1.7.1 Regrading

The topography of the surrounding countryside tends to serve as the recognised pattern for the reclamation grading. Special furrows and diversions can be built into the grading system to prevent rill and gully erosion prior to plant establishment. Slopes up to a maximum of 10^{O} are preferrable with spoil materials in order to reduce surface erosion and slippage. The process of regrading involves the movement of thousands of tonnes of material to create this new land-form and is commonly achieved by the removal of mounds into hollows.

Preliminary sampling before earth-moving may be beneficial as unsuitable material such as that with a high pyritic content or a poor structure, like washery waste, can be identified and buried during the regrading. Failure to sample before grading could also lead to the burial of weathered material that had undergone chemical and physical change and was supporting a natural vegetation cover. Subsequently unweathered material would have been exposed that could break down and become toxic through the oxidation of pyrite (Doubleday 1973).

The large variability of the resultant surface spoil requires extensive sampling to determine the physical and chemical properties of material prior to any treatment (Kimber et al. 1978, Kent 1982). The number of samples taken from an area varies widely, and the usual agronomic pattern of making a composite sample from a number of sub-samples is questionable for colliery spoil because of its heterogeneity. It would be more advantageous to obtain a range of characteristics for the area rather than an average.

Raw shale has very poor soil structure and so is susceptible to compaction at even low moisture contents. In regrading the spoil surface is crossed many times by the heavy earth-moving machinery and therefore the material is likely to become compacted, sheared and smeared which could retard or inhibit root growth. The extent of the deformation increases with increasing moisture content, so the timing of regrading can be of extreme importance (Richardson 1975). As a result it is common practice for the spoil to be ripped to a depth of 20-30 cm prior to any amendment addition.

1.7.2 The use of a soil cover

The reclamation schemes under investigation in this study did not incorporate the use of a soil cover, so this technique is only discussed briefly.

There are many factors associated with colliery spoil that are detrimental to plant establishment; low pH, low nutrient status, high levels of trace metals, high bulk density etc., that have to be corrected by the addition of various amendments. An alternative is to mask this material with a layer of soil that provides a suitable seed bed and increases plant survival.

If soil is available then it is generally spread as a 10-15 cm layer on top of the compacted spoil. The most common source of soil is from the fields surrounding the bing, an area of which is often used at the regrading stage. Importing soil on to a site is unusual due to the very high costs of transportation. The topsoil and subsoil are removed from the field, the bing regraded, and the soil replaced.

Studies by Donovan et al. (1976) and Power et al. (1981) have shown that herbage yield increased as the thickness of soil layer was increased. However Arnold (1981) who also found yield to increase with soil depth, concluded that the quality of the soil was of more importance than quantity.

A 10-15 cm cover of soil is commonly used which is acceptable both economically and in aiding plant establishment (Doubleday 1973). However it does not provide a permanent solution as the spoil influences still occur at depth.

1.7.3 Liming

One of the major chemical constraints to plant establishment on many colliery spoils is the low pH of the waste material. It is common to find pH values of 3 to 4, and on the most acid sites values below 3 can be found. The usual method of improving the spoil conditions is by addition of large quantities of lime. However there is some difficulty in producing a suitable lime requirement figure. The lime requirement to counteract the existing acidity can be calculated using one of the standard agricultural methods. This would then be incorporated to a depth of ~30 cm and would encourage root growth which in turn improves soil structure by the incorporation of organic matter and breaking up heavy spoils.

A problem arises when there is any pyrite present in the surface layers of the spoil as it can be a source of potential acidity. This, plus the natural leaching of lime, can often result in acid regeneration. Therefore when a lime requirement is calculated, this source of potential acidity must be taken into account. Assuming complete oxidation of pyrite, Costigan et al. (1981) have determined that 40 tonnes of $CaCO_3$ pere hectare should be added to neutralise each 1% of pyrite in the spoil. Adding this figure to that for existing acidity results in a total lime requirement. Pulford (1976) has reported pyrite contents of up to 5% in spoils found in central Scotland, and very acid spoils are now being treated with as much as 150 tonnes $CaCO_3$ per hectare (Costigan et al.

1981).

This method has inherent problems due to the heterogeneity of the spoil within one tip. Variation in pyritic content and pH can lead to a wide range of lime requirements. This results in a number of possible liming strategies:

i) Lime the whole site to the maximum value for total acidity that was measured. This assumes that the most pyritic material has been identified, if it has not then there will still be a problem of acid regeneration. In addition the high levels of lime added to any low pyritic material may reduce the effect of fertilisers and cause nutrient imbalances and deficiencies in establishing plants.

ii) Lime the site using a total lime requirement figure obtained from adding an average figure of lime requirement for potential acidity to that for existing acidity. This method can result in acid regeneration in highly pyritic areas.

iii) Highly pyritic areas may be identified and limed at a different rate to the rest, but unless these areas are large and discrete then there will be practical difficulties regarding application of the lime.

iv) Use the lime requirement to counteract existing acidity only with subsequent liming to maintain pH if regeneration occurs. This option requires careful management, and it has been found that surface dressings of lime to re-establish pH at depth are ineffective due to poor percolation (Brown et al. 1956, Bloomfield et al. 1982).

v) Coarse lime material can be applied along with ground limestone at a rate to counteract existing acidity. The coarse material will slowly release lime to neutralise any potential acidity without having any detrimental effects on the low pyritic areas. This approach has encountered difficulties as iron oxide can precipitate on the surface of the limestone lumps and effectively seal them.

The choice of liming strategy depends to a great extent on the chemical variability of the spoil, the after use envisaged, the level of management and maintenance available, and finally the amount of finance that has been allocated to the reclamation project as a whole.

1.7.4 Nutrient application

The deficiency of major nutrients is common to most colliery spoils that are to be reclaimed. This is normally remedied by the application of a single dose of a compound inorganic fertiliser which usually has an N:P:K ratio of 20:10:10 or 20:15:15. This tends to be applied at a rate of 300-500 kg/ha and supplies a readily available source of nitrogen at germination. However the addition of sufficient fertiliser to promote growth is not a long-term solution to the problem of the poor nutrient status of the spoil. Unless a substantial nutrient capital is built up that has the ability to supply nutrients via cycling and mineralisation then the reclamation scheme is likely to fail. Nitrogen loss occurs mainly through leaching and phosphorus can be made unavailable through fixation and adsorption in the spoil.

Bradshaw et al. (1973) found that 626 kg/ha of a 20:15:15 fertiliser established plant cover, but in order to maintain growth further additions of 376 kg/ha in the second and third years were necessary. Gemmell (1973) recommended the application of 20:10:10 fertiliser at 250 kg/ha at seeding with annual applications of 15:15:15 fertiliser at the same rate. However on many sites this was found to be simply maintaining plant growth with no long-term spoil improvement through humus and organic matter build-up.

Thus until a sufficient nutrient capital has been established, the condition of plant growth must be carefully monitored to prevent regression due to nutrient deficiencies.

Obviously high levels of nutrient input are required in the majority of reclamation schemes, and with the ever increasing cost of inorganic fertilisers, other alternative forms of fertiliser have been investigated in order to reduce the cost of reclamation.

The use of organic waste products has received widespread attention, with sewage sludge and chicken manure being the most commonly studied because of their low cost and general availability.

Sewage sludge is a useful source of nitrogen and phosphate, but contains little or no potassium as it is lost in the liquid effluent. The actual levels of nutrients vary greatly depending on the treatment the sludge has received ie. whether it is raw or digested aerobically, and also on the source of the sewage sludge itself. There can be problems of high trace metal content in sludges taken from industrial areas which can lead to difficulties at very high application rates.

As well as being a source of nutrients, sewage sludge can have other beneficial effects when used for reclamation. The organic matter associated with the sludge leads to an improved soil structure resulting in more stable soil aggregates, greater pore size and penetrability and a better water holding capacity (Rimmer and Gildon 1986, Topper and Sabey 1986, Joost et al. 1987). Another advantage of using sludge is that some of the nitrogen is slowly released and so can become available to the plants over 3-5 years (Sopper and Seaker 1983). Sewage sludge applications also stimulate microbial activity (Aldon 1982, Fresquez and Lindemann 1982, Rimmer and Gildon 1986), which is of long-term importance if the inherent fertility of these sites, based on the recycling of nutrients through organic matter, is to be improved.

Poultry manures when used in reclamation have the same beneficial effects as sewage sludge on spoil structure and microbial activity. In addition they tend to stimulate greater vegetation yields (Yam 1984) because of their richer nutrient content. As well as providing more nitrogen and phosphorus, the poultry manures also contain reasonable levels of potassium. The actual content again depends on the type of manure; battery manure (fresh), broiler and deep litter, or dried poultry manure.

Because of their slow releasing properties and other beneficial effects, it has been suggested that the utilisation of organic wastes in combination with inorganic fertiliser may be the most effective and economic practice for waste disposal and derelict land reclamation (Aina and Egdum 1980, Sims and Boswell 1980). An alternative way to provide nitrogen in the rooting zone is by the inclusion of a legume species in the seed mixture as they have the ability to fix nitrogen from the atmosphere. Bradshaw et al. (1973) found that legumes inoculated with N-fixing bacteria fixed 52-112 kg N/ha in a year, while Palmer and Iverson (1983) found white clover (Trifolium repens) to add 146-167 kg N/ha in a year to spoil. However this was reduced under conditions of low phosphate availability.

The proportion of legumes used in the seed mixture varies from 7-15%, and the most frequently sown species are white clover (Trifolium repens) and red clover (Trifolium pratense) because other species such as lupins (Lupinus sp.) and birdfoot trefoil (Lotus corniculatus) are of little use in an arable situation.

A problem with clovers is that they tend to decline with increasing age and become replaced by grass, probably via competitive exclusion due to the improved growth of the grass resulting from the increase in mineralisable nitrogen (Jeffries, Willson and Bradshaw 1981).

1.7.5 Seeding

Seeding is usually caried out by the traditional broadcasting method unless the nature of the material or the topography of the site prevent it. In these cases hydroseeding, where the seed is sprayed on to the site in a slurry containing an organic mulch, fertiliser, and possibly a stabiliser, is often used. Although this would appear to be an ideal method of application, problems have constantly arisen, usually with the failure of clover establishment. Sheldon and Bradshaw (1977) and Roberts and Bradshaw (1983) narrowed the problem down to a toxic interaction between seed, fertiliser and stabiliser. The rates of seed application tend to vary from region to region, but are commonly in the range of about 50-110 kg/ha.

The most common species used in a seed mix for reclamation are shown in Table 1.1 (Kent 1982). The incorporation of a legume species in the seed mix is very important as they can maintain a substantial nitrogen supply for the main grass component of the sward. Because of the lack of any microbial population in raw shale, it is usually necessary to inoculate the legumes with their associated nitrogen-fixing bacteria. Although white clover (Trifolium repens) is the most widely planted and successful species, there are a range of other legumes that could be considered depending on the intended after use of the site (Jeffries, Bradshaw and Putwain 1981, Jeffries, Willson and Bradshaw 1981).

Although the application rates of lime and fertiliser can vary from site to site subject to the spoil properties, each regional body uses more or less the same seed mixture on all sites.

Table 1.1 Grass and legume species most commonly used in spoil reclamation (Kent 1982)

English Name	Latin Name
Common bent	*Agrostis tenuis*
Crown vetch	*Coronilla varia*
Cocksfoot	*Dactylis glomerata*
Meadow fescue	*Festuca pratensis*
Creeping red fescue	*Festuca rubra*
Chewings fescue	*Festuca rubra communitata*
Italian ryegrass	*Lolium multiflorum*
Perennial ryegrass	*Lolium perenne*
Small-leaved timothy	*Phleum bertolonii*
Timothy	*Phleum pratense*
Smooth-stalked meadow grass	*Poa pratensis*
Black medock	*Medicago lupulina*
Birdsfoot trefoil	*Lotus corniculatus*
Alsike clover	*Trifolium hybridum*
Red clover	*Trifolium pratense*
White clover	*Trifolium repens*

1.7.6 General aftercare and maintenance

The problem of aftercare and maintenance is dependent to a great extent on the planned after use of the reclaimed site. Most of the difficulties arise when a good, healthy vegetative cover is required, in which case the site has been reclaimed either for cosmetic purposes or for agriculture. In the case of agriculture a grass crop tends to be the first choice since ploughing is often ruled out because of the high proportion of stone and rock fragments plus the possibility of cables, pipes, rails and foundations being encountered at plough depth.

The most common problem is the regression of plant growth due to the production of secondary acidity with renewed weathering of pyritic materials. Plant failure and reduced yields may also arise from nutrient deficiencies where a sufficient nutrient capital has not been established to supply required nitrogen and phosphorus in the long-term. Remedial action is very difficult and expensive because of the localised nature of these problems, and the differing amounts of lime and nutrients required as a result of the large degree of heterogeneity associated with this type of material.

Bradshaw and Chadwick (1980) have shown that a visual inspection of a site can provide information on possible toxicity and nutrient deficiency problems, but more detailed monitoring is advised by field experiments and chemical analysis.

Where a grass sward has been established and is being used for grazing, the stocking rates and times have to be very carefully managed due to the poor structural nature of the spoil. Poor management can result in complete breakdown of any soil structure that had been developed with the subsequent failure of further vegetative growth.

The success of many reclamation schemes therefore requires regular monitoring and prudent management to ensure that the established vegetation is maintained.

1.8 AIMS OF THE THESIS

As more derelict industrial land is reclaimed the aftercare costs increase and have to be met by the local authority or the land owner. Experience has shown that, while reclamation may initially be successful in terms of vegetation cover and appearance, in the long-term spoil conditions may degenerate and any established vegetation deteriorate. Treatment of such degeneration by repeated applications of lime and fertiliser is expensive. However the use of amendments such as manures could help to alleviate this problem by improving spoil physical conditions and providing a long-term supply of nutrients.

Much of the work in this project was centred on field trials established at Baads Colliery, West Lothian where four organic treatments were used in an attempt to improve the properties of colliery spoil prior to revegetation. The major emphasis of the work was on the build-up of a nutrient capital within the spoil, and the development of nutrient cycling. Attention was also given to the creation of a humified organic component in the spoil and the role of biological activity.

New trials were established at Riddochhill Colliery to compliment the work carried out on the trials at Baads Colliery, and at Loganlea Colliery where the value of various leguminous plant species in reclamation was to be assessed.

CHAPTER 2

FIELD TRIALS

2.1 BAADS COLLIERY

This experiment was set up by J. Devlin in 1980 as part of an on-going reclamation project. The information presented in Section 2.1 and the initial data from these plots were provided by J. Devlin. This field trial, and those at Loganlea and Riddochhill, were carried out in conjunction with the Derelict Land Reclamation Unit of Lothian Regional Council Planning Department.

2.1.1 Initial conditions

After the intial step of regrading had been carried out by the Lothian Regional Council, an area of approximately 3,000 m^2 was allocated to the establishment of the experimental plots.

The raw unburnt shale was systematically sampled and analysis showed a range of pH values from 2.3 to 3.8 and pyritic contents of 0.07% to 2.92%. The levels of extractable nitrogen, phosphorus and potassium were very low, and in most cases undetectable.

2.1.2 Amendments

The chemical nature of the spoil under investigation resulted in there being two aims to the project:

a) The addition of lime to improve the pH status of the spoil, and prevent any acid regeneration in the future.

b) The addition of various organic amendments to improve the physical structure of the spoil and provide a source of nutrients, especially nitrogen and phosphorus, to the establishing vegetation.

The lime requirement to counteract the existing acidity was 25 t/ha ground limestone, but the figure for potential acidity, based on the pyritic content, ranged from 4 to 120 t/ha. A compromise figure of 25 t/ha was therefore taken for potential acidity as this would cope with the acid produced by most of the pyrite figures measured. Thus 50 tonnes of lime per hectare was taken as the total lime requirement for this site. On the trial plots lime additions of 0, 25 and 50 t/ha were used.

Four organic amendments were used on the trial plots: chicken manure, sewage sludge, peat and Alginure (a seaweed based soil conditioner).

Both the manure type amendments, chicken manure and sewage sludge, have been used previously as additions in spoil maintenance as they are a source of plant nutrients and organic matter. Sewage sludge should be freely available from local authorities, and chicken manure can usually be obtained for a nominal fee (£1.00 to £1.50 per tonne for this experiment). The manures are bulky which results in high transportation costs so they are only economically viable if there is a source close to the site being reclaimed.

Peat, although being more inert and chemically poorer than the manures, is still a valuable source of organic matter that may aid in spoil structural development.

Alginure is a purely organic product derived from brown seaweed and has been developed to improve soil structure by stabilising soil crumbs and flocculating clay particles with the result of increased aeration and water retention. The alginure consists of sodium alginate and a black lignin-like substance, which on the addition of water in the presence of calcium ions produces a strong and continuous jelly that acts as the soil stabiliser. Although performing as a soil conditioner, the alginure is a poor source of the three major plant nutrients. The recommended dosage for soils is 2.25 t/ha plus annual maintenance additions of ~0.05 t/ha. This material was obtained from Alginure Products Ltd.

The rates of addition of the amendments were:

Sewage sludge and peat at 0, 5, 10, 20 t/ha;
Chicken manure at 0, 1, 2, 4 t/ha;
Alginure treatment at 0, 2, 4 and 8 t/ha gypsum
plus 0, 0.3, 0.6 and 1.2 t/ha of
both alginure and calcified
seaweed.

Chicken manure was applied at lower rates because of its high nitrogen content.

The combination of the liming rates and organic amendment rates resulted in a total of 39 treatments (Table 2.1). All the treatments were triplicated in plots measuring 8 m x 3 m. Three randomised blocks were set out in the trial area, each containing one plot of each treatment.

Table 2.1 Details of field experiments at Baads

Treatment number	Lime and organic amendment applications t/ha
1	0 lime, 0 organic amendment
2	50 lime, 0 organic amendment
3	25 lime, 0 organic amendment
4	0 lime, 10 peat
5	50 lime, 10 peat
6	25 lime, 10 peat
7	0 lime, 20 peat
8	50 lime, 20 peat
9	25 lime, 20 peat
10	0 lime, 5 peat
11	50 lime, 5 peat
12	25 lime, 5 peat
13	0 lime, 2 chicken manure
14	50 lime, 2 chicken manure
15	25 lime, 2 chicken manure
16	0 lime, 4 chicken manure
17	50 lime, 4 chicken manure
18	25 lime, 4 chicken manure
19	0 lime, 1 chicken manure
20	50 lime, 1 chicken manure
21	25 lime, 1 chicken manure
22	0 lime, 5.2 "Alginure"
23	50 lime, 5.2 "Alginure"
24	25 lime, 5.2 "Alginure"
25	0 lime, 10.4 "Alginure"
26	50 lime, 10.4 "Alginure"
27	25 lime, 10.4 "Alginure"
28	0 lime, 2.6 "Alginure"
29	50 lime, 2.6 "Alginure"
30	25 lime, 2.6 "Alginure"
31	0 lime, 10 sewage sludge
32	50 lime, 10 sewage sludge
33	25 lime, 10 sewage sludge
34	0 lime, 20 sewage sludge
35	50 lime, 20 sewage sludge
36	25 lime, 20 sewage sludge
37	0 lime, 5 sewage sludge
38	50 lime, 5 sewage sludge
39	25 lime, 5 sewage sludge

The cultivation sequence used to etablish the plots in 1980 followed as closely as possible the standard sequence employed by the Lothian Regional Council:

1) Heavy disc harrow to break up any surface compaction.
2) Coarse stone picking which involved removing any debris not passing through a 150 mm ring.
3) Application of limestone.
4) Light disc harrow to work the lime into the top 200 mm of spoil.
5) Preseeding fertiliser, 300 kg/ha 15:10:10 N:P:K spread no sooner than 10 days after liming and 5 days before seeding.
6) Fertiliser worked into the top 50 mm spoil with a light seed harrow.
7) Broadcast standard Lothian Regional Council seed mix (Table 2.2) at a rate of 80 kg/ha.
8) Lightly harrow seed into the top 20 mm of spoil.

Adaptations to this cultivation sequence had to be made because of the small dimensions of the plots:

Lime was applied by hand, after the addition of the NPK fertiliser, and lightly disced into the top 200 mm of spoil. The organic amendments were then added, also by hand, and lightly mixed into the spoil. Seed was broadcast as above.

A year after the plots had been established a maintenance treatment of 5 t/ha ground limestone and 300 kg/ha 15:10:10 N:P:K fertiliser was added to one half of each plot.

Table 2.2 Standard Lothian Regional Council Reclamation Seed mix

50%	Perennial Ryegrass	*Lolium perenne*
25%	Creeping Red Fescue	*Festuca rubra*
9%	Timothy	*Phleum pratense*
10%	Cocksfoot	*Dactylis glomerata*
6%	White Clover	*Trifolium repens*

2.1.3 Plot selection

It was observed that both rates of lime used in the experimental trial raised the pH initially from 3.0-3.5 to 6.5-7.0. After 2 years the pH´s of the plots which had received either 25 t/ha or 50 t/ha lime and no organic amendment averaged 5.7. Thus on these plots the initial lime application made no difference to pH over 2 years and so only the plots receiving 25 t/ha were used in this present study.

The plots receiving the highest rates of the four organic amendments produced the greatest yields and ground cover over the first 2 years and so were chosen for further investigation.

This resulted in six treatments being chosen (Table 2.3) and analysis was carried out on the original half of each plot, and the half that had received the maintenance addition of lime and fertiliser.

Table 2.3 Treatments under investigation from Baads

4	t/ha Chicken Manure	+	25	t/ha Lime
20	t/ha Sewage Sludge	+	25	t/ha Lime
10.4	t/ha Alginure	+	25	t/ha Lime
20	t/ha Peat	+	25	t/ha Lime
No	Organic Amendment	+	25	t/ha Lime
No	Organic Amendment	+	0	t/ha Lime

2.2 RIDDOCHHILL AND LOGANLEA COLLIERIES

The absence of any pyrite in these shales resulted in a low lime requirement of 10t/ha being needed to counteract any existing acidity. As a result the nutrient availability and spoil development capabilities of various spoil treatments could be investigated without any added complications from differing acidity and liming levels.

A total of six hectares was made available by the Lothian Regional Council, four at Riddochhill and two at Loganlea. Larger plots could be used that would be more representative of the whole site, and would enable the standard cultivation sequence to be followed unlike those at Baads Colliery. These facts are important if successful treatments from the plots are to be of any practical use in further reclamation schemes. Three separate trials were established:

2.2.1 Riddochhill I

In this study the nitrogen supplying capabilities of the two most successful treatments from the Baads trials, chicken manure and sewage sludge, were compared against an inorganic fertiliser. The availability of nitrogen, as well as the other nutrients, is essential to stimulate quick growth and provide a dense vegetative cover. The inorganic nitrogen as $(NH_4)_2SO_4$ was applied at two rates, 100 and 500 kg N/ha. The organic amendments were applied at rates to supply the equivalent amounts of "available" nitrogen. These high levels were used to try and provide a sufficient nutrient capital that would enable the system to become self-sustaining. Phosphorus and potassium were added to all the treatments as 500 kg/ha 0:10:10 N:P:K. This ensured no deficiency problems that may have affected any results.

Each treatment (Table 2.4) was carried out in triplicate using plots measuring 15 m x 35 m. The cultivation sequence was similar to the standard method employed at the Baads Colliery with the nitrogen fertiliser and organic amendments being applied after the P:K fertiliser and before seeding. The standard Lothian Regional Council seed mix was used (Table 2.2).

Table 2.4 Riddochhill trial I: Amendment treatments

Inorganic N($(NH_4)_2SO_4$)		100 kg N/ha
Inorganic N($(NH_4)_2SO_4$)		500 kg N/ha
Chicken manure	6.25 t/ha	100 kg N/ha
Chicken manure	31.25 t/ha	500 kg N/ha
Sewage sludge	12 t/ha	100 kg N/ha
Sewage sludge	60 t/ha	500 kg N/ha
Control		0 kg N/ha

2.2.2 Riddochhill II

This trial was established to compare the use of high levels of organic amendments as an alternative to expensive inorganic fertilisers in spoil reclamation. Chicken manure and sewage sludge were applied at the same rates as in the Riddochhill I trial, but these plots received no P:K fertiliser. For the inorganic treatment, 500 and 2,500 kg/ha of 20:10:10 N:P:K fertiliser were used.

One large plot, 35 x 66 m, was set up for each treatment with the intention that these would be subdivided at a later date to undergo various aftercare and maintenance programmes.

2.2.3 Loganlea

The nitrogen fixation capabilities of the leguminous plant species has resulted in their being of great value in many reclamation schemes. They have been shown to increase the nitrogen availability of spoil when grown in pure stands or in association with a grass sward. In this experiment three legumes, white clover, birdsfoot trefoil, and white lupin were sown in pure stands, as well as the white clover and birdsfoot trefoil being sown in association with the Lothian Regional Council standard grass seed mix. Each treatment (Table 2.5) was carried out in triplicate with all the plots receiving 10 t/ha lime and 300 kg/ha 20:10:10 N:P:K fertiliser.

Prior to any cultivation the experimental area was sprayed with a translocated weedkiller to remove any plant species that were established. The standard Lothian Regional Council cultivation sequence was followed.

Table 2.5 Loganlea trial: Legume treatments

White Clover	20 kg/ha
Birdsfoot Trefoil	20 kg/ha
White Lupin	200 kg/ha
Grass mix + 10% White Clover	100 kg/ha
Grass mix + 20% White Clover	100 kg/ha
Grass mix + 10% Birdsfoot Trefoil	100 kg/ha
Grass mix + 20% Birdsfoot Trefoil	100 kg/ha
Grass mix + 5% White Clover + 5% Birdsfoot Trefoil	100 kg/ha

2.2.4 Problems

A number of problems arose following the establishment of these trials that highlighted some difficulties that can be encountered during any reclamation scheme.

At Riddochhill the initial regrading scheme did not leave a sufficient slope or provide any drainage channels with the result that waterlogging occured in several areas with standing water being present throughout most of the year. This retarded plant growth wherever it developed.

An area of burning material was unsuccessfully buried during regrading, and this spread and encroached into a significant area of the trial plots and killed off all vegetation.

The stone picking stage of the cultivation sequence was very poor leaving large stones that restricted growth and can be a problem during any aftercare procedures such as grass cutting. There was also little incorporation of the organic amendments which remained mostly on the spoil surface.

Due to contractual difficulties the cultivation and seeding was not carried out until the September of 1983, and consequently there was almost complete failure of the leguminous plants.

Therefore for a reclamation scheme to succeed, great care has to be taken during each step in the process as failure to carry out one stage in the process can eventually cause complete collapse of the project as a whole.

CHAPTER 3

MEASUREMENT OF ORGANIC MATTER AND MICROBIAL ACTIVITY

3.1 INTRODUCTION

Undisturbed colliery spoil heaps are composed mainly of coarse inorganic materials such as rock wastes from the shafts and underground tunnels as well as shale that is brought to the surface on the extraction of the coal itself. Organic matter is present only in very small amounts and usually in the form of coal or organic material associated with the black shales. In most cases the time elapsed since the dumping of the spoil has not been sufficient to allow any build-up of humified organic matter. The lack of organic matter and the very coarse texture, usually more than 50% of the material is greater than 2 mm diameter, leads to a poor structure that can cause waterlogging in the winter and lack of moisture in the summer (Doubleday 1974). These conditions, as well as the others mentioned in the introductory chapter, have to be overcome before any revegetation can take place.

The introduction of organic matter into the spoil improves the structure, and hence increases the spoil stability and water holding properties, adds to the cation exchange capacity and provides a supply of plant nutrients such as nitrogen and phosphorus.

Ideally this organic fraction should be built up as quickly as possible to provide an environment suitable for plant establishment and growth. In the long-term organic inputs from decaying vegetation play the most important role in improving spoil conditions, but this can be supplemented by the use of organic amendments, such as manures, which will act as a source of nutrients, help initiate microbial activity and improve spoil physical conditions prior to seeding.

The development of a reclamation site is dependant to a large extent on the build-up of an organic matter fraction within the spoil. The experimental plots at Baads Colliery, West Lothian have been operational for four years and so it is of great interest to determine the degree to which organic matter has built up and also to compare the effect of each organic amendment. It is important to note that in the measurement of organic matter, the method must distinguish between the "humified" organic matter that is of interest and the organic material associated with the spoil components. This chapter examines the ability of both chemical and biological methods to measure organic matter in colliery spoil.

3.1.1 Review of chemical methods for measuring organic carbon and organic matter

The measurement of organic matter in colliery spoil is usually carried out using standard soil techniques. The most common of these methods are reviewed with specific methods being selected for determining organic matter in a background of carbon bearing material.

Total carbon, which is a combination of organic carbon found mainly in organic matter, and inorganic carbon derived from carbonate minerals, can be determined by either wet or dry combustion (Allison et al. 1965). Wet combustion uses a mixture of $K_2Cr_2O_7$, H_2SO_4 and H_3PO_4 in a closed system flushed with CO_2-free air, while in dry combustion a soil-catalyst mixture is heated in a furnace in a stream of O_2 or CO_2-free air. In both cases CO_2 is liberated, trapped and measured. The organic carbon can then be calculated by subtracting the inorganic carbon from total carbon. The methods for measuring total carbon are very severe and include the highly carbonised materials such as charcoal and coal. Due to the relatively high background levels of these compounds in colliery spoil these methods would be of limited use in determining the build-up of "humified" organic carbon.

Organic carbon can also be measured by rapid dichromate oxidation techniques. This was first proposed by Schollenberger (1927) in which organic matter is oxidised by a hot mixture of $K_2Cr_2O_7$ and H_2SO_4.

$$2Cr_2O_7^{2-} + 3C^0 + 16H^+ \ -> \ 4Cr^{3+} + 3CO_2 + 8H_2O \qquad (1)$$

Any dichromate reduced by reaction with the soil is taken to be equivalent to the organic carbon present in the sample. Since Schollenberger's initial experiment, various authors have modified the concentrations of dichromate and acid in the oxidation mixture (Table 3.1) in an attempt to get more efficient oxidation. These concentrations lie within a fairly close range and there

Table 3.1 Digestion reagents used in various rapid dichromate methods for organic C determinations (Nelson and Sommers 1982)

Method	Digestion Reagent Concentration		
	N		
	$K_2Cr_2O_7$	H_2SO_4	H_3PO_4
Schollenberger (1927)	0.35	36	-
Tyurin (1931)	0.4	18	-
Walkley and Black (1934)	0.33	25	-
Anne (1945)	0.16	22	-
Tinsley (1950)	0.4	15	9
Mebius (1960)	0.267	20	-
Kalembasa and Jenkinson (1973)	0.2	18	5
Nelson and Sommers (1975)	0.4	21.6	-

is no clear evidence that would distinguish one as being better than the rest.

The majority of dichromate oxidation techniques use an external source of heat. Investigations have highlighted the importance of controlling the time and temperature of heating, Tyurin (1931), Schollenberger (1945) and Jackson (1958). Other authors have proposed that the time of heating should be extended from 5-10 mins to 20 mins - 2 hours to ensure complete oxidation of the organic carbon (Tinsley 1950; Mebius 1960).

On the other hand, Walkley and Black (1934) suggested that the heat of dilution of H_2SO_4 is enough to oxidise the organic matter, but not all of the organic compounds found in the soil react, only the most active. As only an average 76% of the organic carbon is recovered a correction factor of 1.32 has to be applied to account for the discrepancy. Various authors have tested the percentage recovery using the Walkley and Black method (Table 3.2) and shown that it varies widely depending on the soil used. The diversity of the correction factors means that the use of an average value can give only approximate levels of organic carbon in the soil.

Certain elements found in soil can lead to interferences in the dichromate oxidation procedure. Cl^- and Fe^{2+} if present consume a fraction of the $Cr_2O_7^{2-}$ giving high values for organic carbon. These can be removed by washing with water for the Cl^- and air drying to oxidise the Fe^{2+} to Fe^{3+}. Higher oxides of manganese, mainly MnO_2, will compete with the $Cr_2O_7^{2-}$ and oxidise

Table 3.2 Correction factors for organic C not recovered by the Walkley and Black method as determined for surface soils by various investigators (Nelson and Sommers 1982)

Reference	No. of soils studied	Organic C recovery		Average conversion factor
		range	average	
		-------- % --------		
Bremner and Jenkinson (1960)	15	57-92	84	1.19
Kalembasa and Jenkinson (1973)	22	46-80	77	1.30
Orphanos (1973)	12	69-79	75	1.33
Richter et al. (1973)	12	79-87	83	1.20
Nelson and Sommers (1975)	10	44-88	79	1.27

some of the organic substances and so give low results for organic carbon.

Values obtained for organic carbon, by any method, can be converted to give an estimate of organic matter by the use of a conversion factor. The factor of 1.724 has been used mostly, with the presumption that organic matter contains 58% carbon. However this factor varies from soil to soil and there can even be a difference between surface and subsurface horizons (Broadbent 1953). It is of more value therefore to report any results obtained by dichromate oxidation as percentage organic carbon rather than changing them to values of percentage organic matter by the use of a rough conversion factor.

It is possible to measure organic matter directly by destroying it and measuring the loss in weight. The two most common methods are hydrogen peroxide treatment (Robinson 1927), and loss on ignition at high temperature (Sobek et al. 1978; Severson and Gough 1983). The peroxide treatment does not oxidise organic matter completely but can be of use in comparing the levels of easily oxidisable organic matter between soils. The loss on ignition method completely oxidises the organic matter, but can also affect inorganic components such as hydrated alumino-silicates, loose structural water and carbonate minerals so giving weight losses in excess of the organic matter. It has been observed that lower temperatures, 350-450^{o}C, can be used to break down the organic matter without altering the inorganic constituents (Ball 1964; Davies 1974).

3.1.2 Microbial techniques

The use of microbial techniques to estimate the amount of organic matter present within a soil is based on the assumption that the organic matter is the main source of essential nutrients and energy for the microbial organisms present within the soil. Since the organisms rely to a great extent on the presence of dead plant and animal remains along with humified organic matter, these microbial techniques should be able to differentiate between these forms of organic matter and the highly carbonised forms found as an integral component of coal spoil.

There are essentially two possible approaches to the measurement of biological activity and hence the presence of humified organic matter. The total microbial biomass can be measured directly, or the basal microbial respiration can be monitored.

Of the methods that determine microbial biomass directly, the most commonly used is that of Jenkinson and Powlson (1976). This is based on soil fumigation, usually with chloroform, followed by re-inocculation and the subsequent flush in microbial activity being used as a measure of the soil biomass. A portion of non-fumigated soil is incubated in the same manner as the fumigated soil, and the difference in the amounts of CO_2-C evolved being used to calculate the soil biomass. There are a few basic assumptions intrinsic to the use of this method which have been summarised by Jenkinson and Ladd (1981). The main ones are:

1) Carbon in dead organisms is more rapidly mineralised than that in living organisms.
2) Fumigation leads to a complete kill.
3) Death of organisms in the unfumigated soil is negligible compared with that in fumigated soil.
4) The only effect of soil fumigation is to kill the biomass.
5) The fraction of dead biomass C mineralised over a given time period does not differ in different soils.

As an alternative to soil fumigation, some authors use glucose as a readily decomposable substrate with the subsequent stimulation in CO_2 respiration being used to calculate biomass (Anderson and Domsch 1978b).

The quantitative extraction of compounds particular to the microbial community such as ATP (Paul and Johnson 1977) have been used to determine microbial biomass. However there are difficulties in transferring data from ATP assays into biomass figures as the ATP content of cells varies under different environmental and nutritional conditions.

The second microbial technique that can be used to determine levels of humified organic matter is that of monitoring the basal soil respiration rate. This can either be carried out in the field or in the laboratory. The activity of the micro-organisms in soil varies greatly under differing conditions of moisture, temperature and aeration so measurements taken in the field where the environment is continually changing are therefore hard to determine and interpret. In the laboratory however the moisture content, temperature and aeration status can be strictly controlled enabling easier interpretation of results and comparison of treatments. For this reason only laboratory based techniques will be discussed.

For the measurement of microbial respiration rates, the soils are incubated under stipulated conditions and the amount of oxygen consumed or carbon dioxide released is measured. There are two basic types of respirometer that are used to measure oxygen consumption. The first is based on the Warburg, Barcroft or Gibson respirometers (Jenkinson and Powlson 1976; Casida 1977; Lawrey 1977) where the partial pressure of oxygen continuously drops and the amount of oxygen consumed is measured either manomerically or volumetrically with manual reading and resetting.

In the second method, the partial pressure of oxygen in the air mixture remains constant by replacement from oxygen produced by the electrolytic decomposition of H_2SO_4 or $CuSO_4$. The amount of oxygen produced and hence consumed by respiration is determined by the amount of current used in the decomposition process. These methods are generally automated and their use with soil is described in Bird and Melville (1969), Sonoda et al. (1972), and Wilson and Griffin (1975a,b).

There are several techniques available for the determination of carbon dioxide evolved during respiration. The simplest uses an aqueous solution of alkali to trap the carbon dioxide which can subsequently be measured. Adding an excess of barium chloride causes the precipitation of barium carbonate which is collected, washed, dried and weighed (Landa and Fang 1978). Titrimetric analysis of the trapped carbon dioxide can be used which combines simplicity with a high degree of sensitivity (Jenkinson and Powlson 1976; Ausmus and O´Neill 1978; Landa and Fang 1978). The absorbed carbon dioxide is calculated by measuring the volume of 0.05 M hydrochloric acid required to reduce the pH of the alkali solution from 8.3 to 3.7. One millilitre of the acid being equivalent to 0.6 mg of carbon. Another method is to measure the change in resistance of the alkali solution as it absorbs the carbon dioxide, or the difference in conductivity before and after the alkali has been exposed to the respiring soil.

3.2 MATERIALS AND METHODS

3.2.1 Chemical methods

The objective of this work was to decide on a simple method of determining organic matter in colliery spoil that would differentiate between the background carbonised material and the humified organic matter which is of interest in any reclamation scheme.

Colliery spoil samples were collected from two sites in central Scotland for comparison with soils of typical organic content that are found under grassland. The spoils were predominantly black shale and had no vegetative cover and received no organic amendment. The soil samples were taken from the surface horizons of soils in the Dunlop series (Mitchell and Jarvis 1956) at two sites, again in central Scotland. Samples of spoil supporting differing levels of vegetation and having received various organic amendments were taken from Baads Colliery, West Lothian. For the experiment using different levels of vegetation a subjective estimation of growth was used, zero, poor and good establishment. These samples were taken from an area outside the trial plots receiving similar cultivation treatments. Samples from within the trial plots were used to compare the effect of various organic amendments on the build-up of organic matter. The trial plots are described in Chapter 2.

Initial studies attempted to measure the organic matter fraction directly by loss on ignition and peroxidation. The technique for loss on ignition was based on the method employed by the Soil Survey of England and Wales (Avery and Bascomb 1974). It has been shown that lower temperatures, 350-450°C, can be used without altering any inorganic constituents (Ball 1964; Davies 1974) so a range of temperatures from 400-750°C was used to observe what effect, if any, the lower temperatures had on the shales and highly carbonised material within the spoil.

Hydrogen peroxide does not completely break down all forms of organic matter, only the highly oxidisable forms. Weight loss was measured by treating a known weight of spoil with 25 cm^3 of 30% hydrogen peroxide for a set time. After treatment the sample was dried at 110°C and re-weighed to determine the loss of active organic matter.

Two methods of dichromate oxidation were undertaken, one with and one without an external source of heat. Studies have shown that the Walkley-Black method attacks very little of the highly carbonised forms of organic matter (Walkley 1947; Bremner and Jenkinson 1960). The standard Walkley-Black method of Hesse(1971) was used with variation in time of reaction from 15-120 minutes.

The Tinsley method (ADAS 1981) was chosen as an example of dichromate oxidation using an external source of heat. Both the time, 5-210 minutes, and temperature, 100°C and 135°C, were varied in an attempt to reduce the effect that the Tinsley method had on the highly carbonised background material.

3.2.2 Microbial methods

The measurment of the basal soil microbial respiration rate was used in an attempt to compare the levels of humified organic matter that had accumulated in spoil having received different amendments. This assumed that the organic matter was the only source of nutrients and energy for the microbial population. Under laboratory controlled conditions, the temperature and moisture content can be kept constant so enabling any differences in respiration rate to be due to varying levels of substrate within the spoil.

The amendment trial plots at Baads Colliery, West Lothian were used for this experiment. Duplicate spoil cores 10 cm in diameter and 15 cm deep were taken from six treatment plots (Table 2.3) in the three areas A, B and C. The samples were air-dried sufficiently to pass through a 4 mm sieve and any discrete pieces of dead roots or unhumified vegetation were removed. Any excessive drying may have affected the availability of the organic matter and altered the microbial population. The sieved material was stored at 2°C in sealed polythene bags until required.

Prior to incubation the spoil pH in water (1:2.5) was measured using a glass electrode and the percentage moisture (110°C) and moisture content at -0.5 bar soil water potential were calculated.

To measure the basal respiration rate a simple incubation using aqueous alkali to absorb any evolved carbon dioxide was set up. A portion of moist spoil equivalent to 50 g oven-dry material was weighed into a 500 ml wide-neck jar. Water was added to each sample to bring the moisture content up to -0.5 bar soil water potential. A small beaker containing 20 ml of 1 M sodium hydroxide was placed inside each jar which was then sealed and incubated at 25°C in the dark. After seven days the beaker containing the sodium hydroxide was removed, the spoil aerated for 6 hours, returned to -0.5 bar moisture and a fresh portion of alkali added. The jars were re-sealed and returned to the incubation chamber. This sequence was repeated for another nine weeks.

During the incubation period any carbon dioxide evolved from microbial respiration would be absorbed by the aqueous alkali. This absorbed carbon dioxide can be measured by various means, but a simple and highly sensitive method is the titrimetric technique described by Jenkinson and Powlson (1976).

1 ml of 1 mg/ml carbonic anhydrase was added to the sodium hydroxideprior to titration giving a steadier end-point to the reaction:

$$Na_2CO_3 + HCl \longrightarrow NaHCO_3 + NaCl \qquad (2)$$

The pH of the alkali was reduced to 10 using 4 M HCl, then to exactly a pH of 8.3 with 0.05 M HCl. At this stage all the carbonate had been converted to bicarbonate (reaction (2)). Further addition of 0.05 M HCl breaks down the bicarbonate releasing carbon dioxide (reaction (3)):

$$NaHCO_3 + HCl \longrightarrow H_2O + NaCl + CO_2 \qquad (3)$$

The titration was continued until the end-point was reached at a pH of 3.7 by which time all the bicarbonate had disappeared. The quantity of carbon dioxide absorbed by the alkali was calculated using the volume of 0.05 M HCl required to reduce the pH from 8.3 to 3.7. 1 ml of 0.05 M HCl being equivalent to 0.6 mg of carbon. The results for microbial respiration can then be expressed as mg carbon evolved per kg of oven-dry spoil.

3.3 RESULTS AND DISCUSSION

3.3.1 Chemical methods

3.3.1.1 Loss on ignition

The direct measurement of organic matter in a soil by loss on ignition is limited to an approximate value as other constituents may be lost in the heating process, leading to an overestimation of the percentage organic matter present. These problems would also manifest themselves by the combustion of unburnt, black colliery spoil. The use of lower temperatures of combustion can eliminate the problems associated with the inorganic fraction and so loss on ignition was carried out at 400, 600 and 750°C. It was thought that the use of these lower temperatures may also leave the highly carbonised materials such as coal and charcoal untouched when the loss on ignition was carried out on coal spoil. This would enable the identification of any build-up of humified organic material during a reclamation scheme. Table 3.3 shows the result of increasing temperature on two soil samples and two spoil samples. The two soil samples were taken from the surface horizon of soils in the Dunlop series that have been under permanent grass. They show the typical pattern of an increasing loss on ignition with increasing temperature. The two spoil samples which were loose, black shales supporting no vegetation and having received no organic treatment responded in the same way as the soils. Of more importance is the fact that even at the lowest temperature, the percentage loss on ignition of the coal spoil was similar to that of the soil. Since there is no apparent source of "organic matter" in these samples, the loss must have been due entirely to the combustion of organics held within the black shale and any coal or charcoal that was present and which contributed nothing to the improvement of nutritional or physical conditions in the spoil.

Table 3.3 Effect of temperature of ignition on weight loss measured

	Loss on ignition (%)		
	Temperature of ignition °C		
Sample	400	600	750
Spoil 1	14.5	21.3	22.7
Spoil 2	15.2	18.8	20.9
Soil 1	17.9	21.0	23.4
Soil 2	18.4	21.6	22.1

Loss on ignition, therefore, can not be used to differentiate between humified organic matter and the background organic fraction that is found in colliery spoil. However it may be possible to use this method for comparing the effect of various reclamation schemes on the establishment of an organic matter fraction by measuring the total loss on ignition of a control sample of bare spoil with that of a sample that has been treated in a reclamation scheme. The trial plots at Baads Colliery, West Lothian gave an opportunity to test this hypothesis. The plots had been established for four years and had received different organic amendments as well as a range of lime additions. The treatments led to a wide variety of vegetation yields hence leading to the accumulation of differing amounts of dead plant and root tissue. The difference between the loss on ignition values of the bare, untreated spoil and those of the amended spoil could then give an indication of the accumulation of humified organic matter in the spoil. However the results (Table 3.4) did not support this theory. The untreated spoil gave the highest value of loss on ignition suggesting that the background material masked any effect due to the build-up of a humified component. Within each amendment, the plot that had received lime and hence had a better vegetation yield, also had the lower loss on ignition. These plots were randomly distributed over a set area, so the differences observed with the vegetation yields could merely be due to the heterogeneity of the spoil material. However, of the six treatments, all showed the trend of decreased loss on ignition in the limed plot. Therefore it is possible that the the input of lime resulted in a dilution of the dense organics associated with the shale and hence a reduction in the percentage loss on ignition.

Table 3.4 Loss on ignition in spoils receiving different treatments and supporting different vegetation covers

Treatment	Loss on ignition at 750°C (%)
No organic, limed	25.6
No organic, unlimed	28.1
Chicken manure, limed	22.8
Chicken manure, unlimed	27.0
Sewage sludge, limed	25.8
Sewage sludge, unlimed	26.7
Peat, limed	24.5
Peat, unlimed	25.0

In an attempt to reduce the effect of the inherent problem of heterogeneity associated with coal spoils, sample cores were taken under various degrees of vegetation cover. The cores were split into two halves which should be similar, apart from any humified organic matter present in the surface portion that has arisen from old vegetation. The results, presented as the mean of duplicate measurements, (Table 3.5) show that for the bare spoil the upper and lower halves of the core gave almost identical values for loss on ignition, indicating good homogeneity within the cores. For the cores under vegetation there is very little difference between the upper and lower halves of the cores. The plots with vegetatation had received a lime treatment and a slight dilution effect in the surface material can be seen apart from the sample labelled "Good Vegetation 1" where the subsurface portion of the core had a much lower loss on ignition. This may be assumed to be because the material in this plot was of a different origin containing some combusted material. The high levels of background organics again make it impossible to identify any build-up of a humified organic component in the spoil.

Table 3.5 Loss on ignition at 750°C of surface and subsurface spoils supporting different vegetation covers

Vegetation cover	Loss on ignition at 750°C (%) Surface (0-6 cm)	Subsurface (6-12 cm)
No vegetation 1	31.8	32.1
No vegetation 2	30.3	31.9
Poor vegetation 1	24.4	25.8
Poor vegetation 2	26.3	32.0
Good vegetation 1	23.0	13.9
Good vegetation 2	31.8	32.2

3.3.1.2 Peroxidation

An alternative approach to determining the quantity of organic matter within a soil or spoil is to oxidise it using hydrogen peroxide and measure the ensuing loss in weight. It has been observed that in soils, the peroxide treatment does not affect any highly carbonised forms of organic matter and appears only to oxidise the active fraction (Nelson and Summers 1982). This method should then lend itself to the measurement of a humified fraction within coal spoil. Peroxide has previously been used for determining pyrite in colliery spoil and the evidence showed that the reaction is initially slow and then violent after a few minutes. The explanation for this has been that there is a short delay before the peroxide penetrates the shale. Since the peroxide has the ability to penetrate the lattices, an experiment was designed to determine whether it could oxidise the background organics found within this fraction of the coal spoil. A portion of both spoil and soil were ground to pass through a sieve of pore size 180 µm. The weight loss of these samples were compared to the less than 2 mm fraction of the same material. There was no effect of grinding on the soil sample (Table 3.6) but with the spoil there was an increased weight loss. Grinding resulted in a greater surface area exposed to the peroxide, resulting in a higher weight loss which suggests that the peroxide had the ability to oxidise the organic material held within the shale material. This makes the use of the hydrogen peroxide method unsuitable for the determination of organic matter accumulation in coal spoil as it is unable to differentiate between this fraction and the background material held within the shale.

Table 3.6 Effect of fineness of grinding on weight loss following peroxidation

Sample	Mesh size	Weight loss following peroxidation (%)
Colliery spoil	2 mm	7.2
Colliery spoil	180 µm	9.0
Soil	2 mm	13.2
Soil	180 µm	13.3

3.3.1.3 Dichromate oxidation methods

Of the numerous techniques designed to use dichromate as an oxidising agent for organic carbon in soils, two methods were chosen in an attempt to measure the same fraction in colliery spoil. The method employed by Walkley and Black does not attack all forms of organic carbon and was chosen in the hope that it would not oxidise any of the background organic carbon found in black colliery shale. The Tinsley method was chosen from those that use an external source of heat in the reaction. These procedures are generally more vigorous and tend to attack most forms of organic carbon so the Tinsley was initially used as a comparison to the Walkley-Black.

Two samples of colliery spoil and two soils were treated using the Walkley-Black and Tinsley methods (Table 3.7). Both soils and spoils showed similar organic carbon contents using both methods, with the Tinsley method giving higher results as would be expected. The increase in the colliery spoil was higher indicating the presence of greater amounts of unreactive organic carbon. Neither method could be used to determine an organic carbon build-up as the colliery spoil used was loose black shale with no source of humified organic matter.

Table 3.7 Comparison of Walkley-Black and Tinsley methods for organic determination in colliery spoil and soil

Sample	Organic matter (%) = (%C x 1.72) Walkley-Black %C	 Tinsley %C
Soil 1	6.8	8.4
Soil 2	11.8	9.8
Colliery spoil 1	6.3	9.2
Colliery spoil 2	9.8	16.9

Attempts were made to modify both techniques in order to reduce the oxidising effect on the background organic material. If this could be done without altering the ability of dichromate to oxidise the humified organic carbon found in the soil then there would be a possibility of discriminating between this and the organics found in the spoil. In the Walkley-Black procedure, the time of reaction was varied between 15 and 120 minutes (Table 3.8). Both the soil and spoil were relatively insensitive to time of reaction. For the Tinsley method both time and temperature of reaction were altered (Table 3.9). The spoil material appeared insensitive to the increase in temperature up to 15 minutes′ reaction time, but thereafter the rise in temperature caused more organic carbon to be oxidised. Increasing the time of reaction produced an elevated oxidation of organic carbon at both temperatures until 110 minutes when the reaction reached its end point. The soil reacted in a similar manner suggesting that the modifications of time and temperature were affecting the oxidation of the humified organic fraction that is of prime interest. The use of either of these two dichromate oxidations is ruled out because both appear to be attacking the background shale which will mask any effect due to organic accumulation.

Table 3.8 Effect of reaction time on organic matter determination by the Walkley-Black method

Time of reaction (min)	Organic matter (%) = (%C x 1.72) Spoil	Soil
15	9.4	10.8
30	8.6	11.2
60	9.3	11.7
120	9.8	11.7

Table 3.9 Effect of reaction time and temperature on organic matter determination by the Tinsley method

Time and temperature of heating		Organic matter (%) (% x 1.72) Spoil	Soil
5 min	100°C	13.5	5.7
5 min	135°C	13.9	7.1
15 min	100°C	17.9	7.2
15 min	135°C	17.9	8.7
30 min	100°C	21.6	7.3
30 min	135°C	22.5	11.2
70 min	100°C	23.3	7.8
70 min	135°C	26.3	13.0
110 min	100°C	24.1	8.3
110 min	135°C	29.2	15.6
140 min	100°C	24.3	8.4
140 min	135°C	30.1	16.0
210 min	100°C	24.7	8.8
210 min	135°C	30.7	15.9

3.3.2 Microbial method

The decomposition of organic matter in the soil is primarily a biological process and carbon dioxide is one of the end-products which can be conveniently measured. Practically all the carbon dioxide evolved from soils which are not supporting a crop is derived from this source. Consequently, carbon dioxide production has long been regarded as a good index of organic matter decomposition in soils (Millar et al. 1936). An incubation experiment to monitor the basal respiration activity of the soil microbes was chosen for two reasons:

1) Under laboratory conditions the moisture content and temperature of the incubating spoils could be strictly controlled, with the ensuing levels and rates of carbon dioxide production giving an indication of organic matter accumulation as well as a comparison between treatments used in a reclamation scheme.
2) The mineralisation of major nutrients such as nitrogen, phosphorus and potassium could be measured at the same time.

The measurement of microbial respiration does not give a direct value of organic matter present within a soil or spoil, but since the microbes depend almost entirely on the organic matter for energy and nutrients the respiration rate should be a good indication of organic matter content. The species of microbe and nutrient content of the organic matter can both have an effect on the rate of organic matter decomposition. However, since the experimental plots under investigation had been established for four years prior to sampling with no fresh source of organic matter being added save that from the growing vegetation, it has been assumed for the purpose of this experiment that these factors had no effect. This would then permit a treatment comparison with a higher rate of carbon dioxide production indicating the presence of a greater level of organic matter. The levels of carbon dioxide production obtained from the experimental plots of the reclaimed colliery spoil could also be compared to those of soils with known organic matter percentage that had been incubated under the same temperature and moisture regimes. Although a direct comparison is not possible due to differing microbial populations, it should be possible to get a rough indication of what levels of organic matter are present in the colliery spoil. This approach should also have the ability to differentiate between any organic matter accumulation brought about by the reclamation scheme and the background organics present within the colliery spoil material itself.

Sampling took place at the end of the growing season (September) of two years, 1983 and 1984. Prior to the incubations, the pH (water), and the moisture content at -0.5 bar soil water potential were measured (Tables 3.10 and 3.11). There was variation in the pH values of all the samples, with as much variation between plots of the same treatment as between the treatments themselves. Most pH values in the limed plots were above pH 5 with the few exceptions being over 4 which caused no apparent reduction in microbial activity. Even the limed sample with a pH of 2.8 from 1983 showed no reduction in activity in comparison to the other samples from that treatment. The values of pH and moisture content obtained highlighted the extreme heterogeneity of the material under investigation which made the evaluation of results very difficult.

Table 3.10 pH and moisture content of spoils sampled in 1983

	pH			% H_2O at -0.5 bar		
Treatment	A	B	C	A	B	C
Chicken Manure	6.8	7.1	6.4	22.6	28.4	28.3
+ Lime	6.6	6.9	6.1	24.1	23.2	19.2
Sewage Sludge	5.3	6.6	6.0	25.2	28.2	27.4
+ Lime	7.0	5.8	5.1	26.4	27.3	26.3
Alginure	6.2	6.4	6.0	23.5	26.4	21.0
+ Lime	6.5	6.5	6.1	24.8	25.5	24.5
Peat	5.2	6.9	6.5	25.7	27.0	26.6
+ Lime	4.6	6.8	6.3	23.2	30.2	23.3
No Amendment	6.0	6.0	2.8	27.6	23.6	26.2
+ Lime	6.5	5.4	4.2	25.4	25.2	27.1
No Amendment	3.0	2.8	3.2	21.3	23.6	21.9
+ No Lime	2.8	2.8	3.2	22.9	25.7	21.1

Table 3.11 pH and moisture content of spoils sampled in 1984

	pH			% H_2O at -0.5 bar		
Treatment	A	B	C	A	B	C
Chicken Manure + Lime	7.3	6.2	7.2	26.9	23.8	27.2
	6.8	6.9	6.9	25.0	26.6	26.8
Sewage Sludge + Lime	6.5	6.3	6.8	34.2	27.7	28.1
	7.3	7.1	5.2	26.3	23.6	27.1
Alginure + Lime	7.1	6.9	5.4	26.5	27.9	25.4
	7.2	6.8	5.5	23.8	28.3	27.1
Peat + Lime	4.5	6.7	7.2	24.1	28.8	28.3
	4.6	7.2	6.9	25.8	34.1	28.6
No Amendment + Lime	7.1	7.0	7.2	22.4	22.9	24.4
	4.8	7.2	4.7	21.3	21.0	23.9
No Amendment + Lime	2.7	3.2	2.9	24.2	25.7	22.8
	2.8	2.9	3.1	24.7	26.4	22.6

The total cumulative levels of carbon dioxide evolved during the ten week incubation for the years 1983 and 1984 are shown in Figures 3.1 and 3.2 respectively (averages of areas A, B and C).

Figure 3.1 Cumulative CO_2 evolution (mg C/kg spoil) over ten weeks (1983)

Figure 3.2 Cumulative CO_2 evolution (mg C/kg spoil) over ten weeks (1984)

Figure 3.3 Weekly CO_2 evolution (mg C/kg spoil) over ten weeks (1983)

Figure 3.4 Weekly CO_2 evolution (mg C/kg spoil) over ten weeks (1984)

Figure 3.1

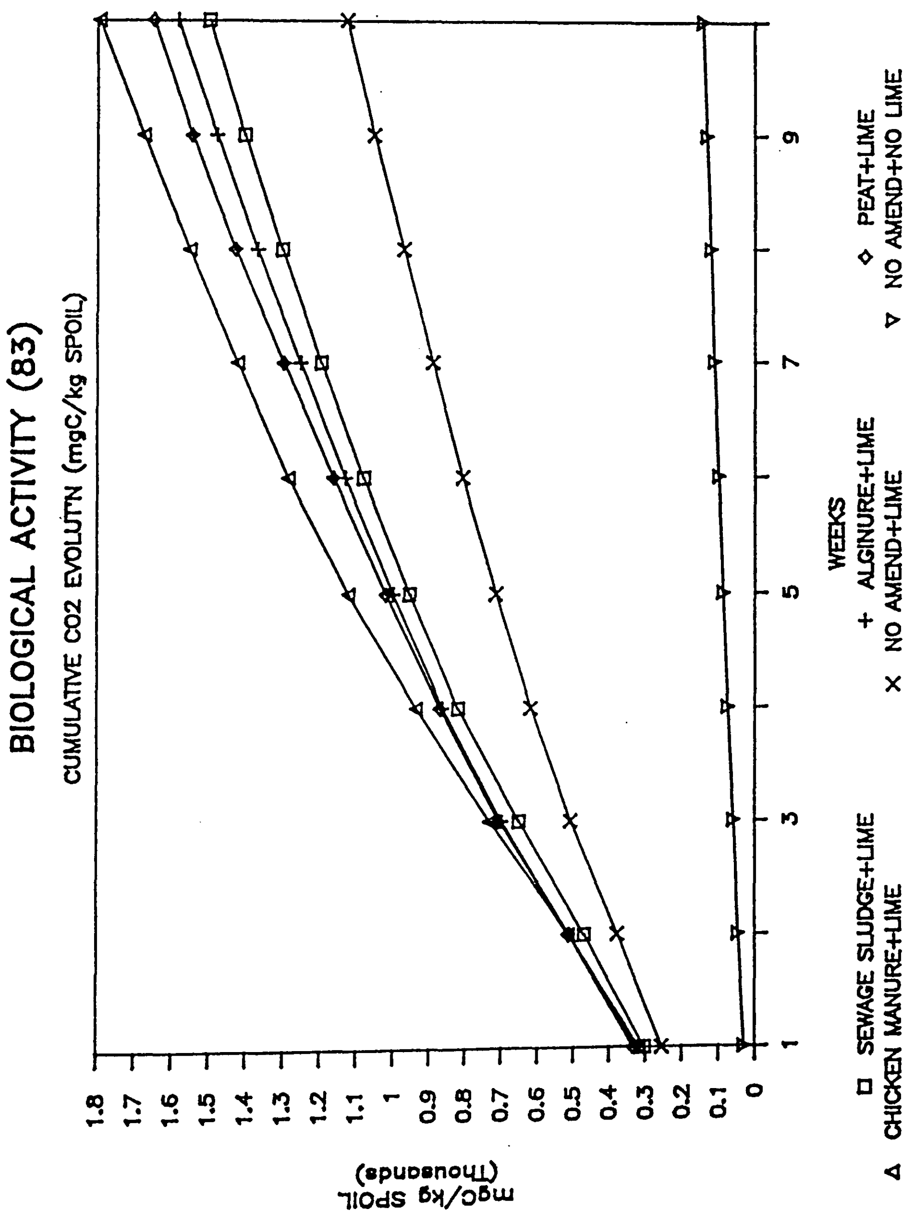

BIOLOGICAL ACTIVITY (83)
CUMULATIVE CO2 EVOLUTN (mgC/kg SPOIL)
mgC/kg SPOIL
(Thousands)
1.8
1.7
1.6
1.5
1.4
1.3
1.2
1.1
1
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0
1
3
5
7
9
WEEKS
□ SEWAGE SLUDGE+LIME
+ ALGINURE+LIME
◇ PEAT+LIME
Δ CHICKEN MANURE+LIME
× NO AMEND+LIME
∇ NO AMEND+NO LIME

Figure 3.2

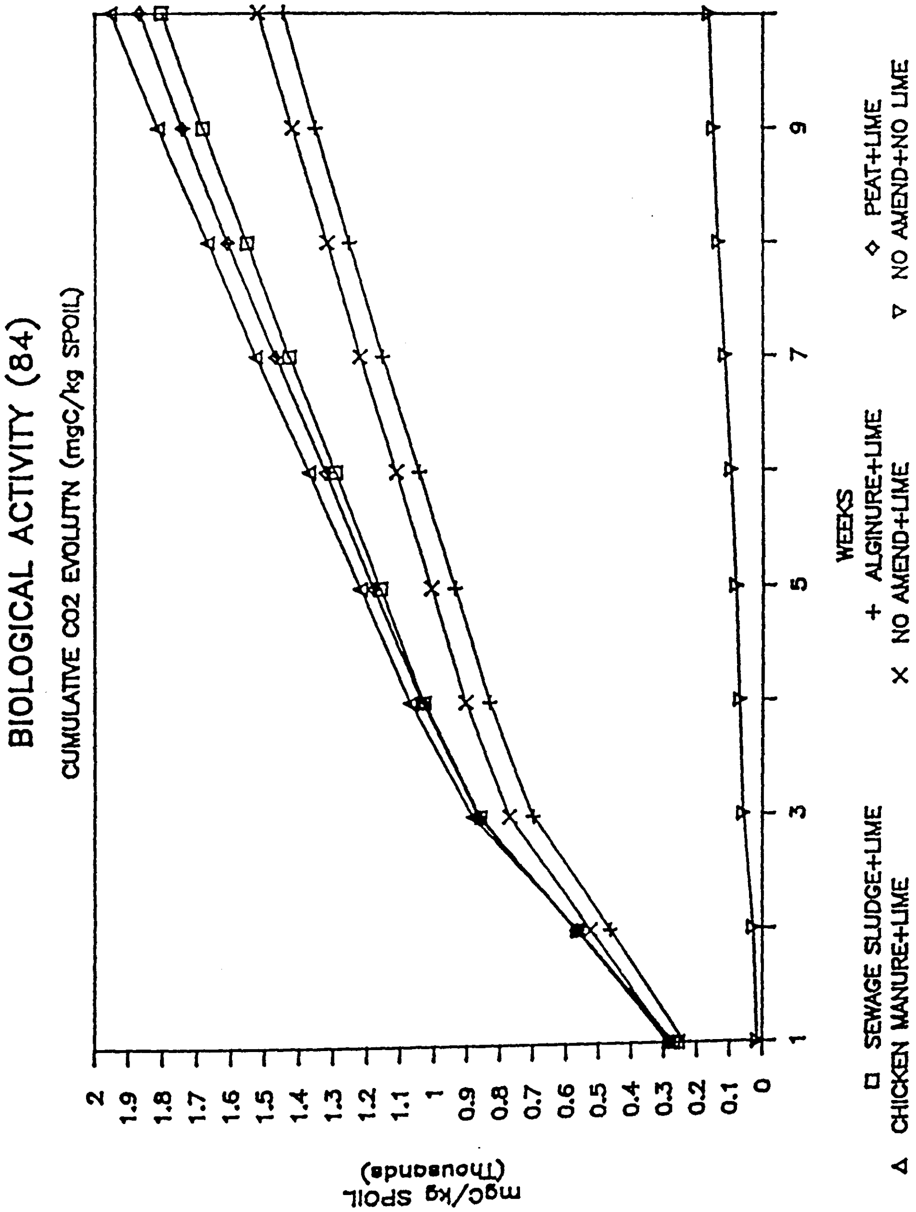

BIOLOGICAL ACTIVITY (84)
CUMULATIVE CO2 EVOLUTN (mgC/kg SPOIL)
mgC/kg SPOIL
(Thousands)
2
1.9
1.8
1.7
1.6
1.5
1.4
1.3
1.2
1.1
1
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0
1
3
5
7
9
WEEKS
□ SEWAGE SLUDGE+LIME
+ ALGINURE+LIME
◇ PEAT+LIME
△ CHICKEN MANURE+LIME
× NO AMEND+LIME
▽ NO AMEND+NO LIME

Figure 3.3

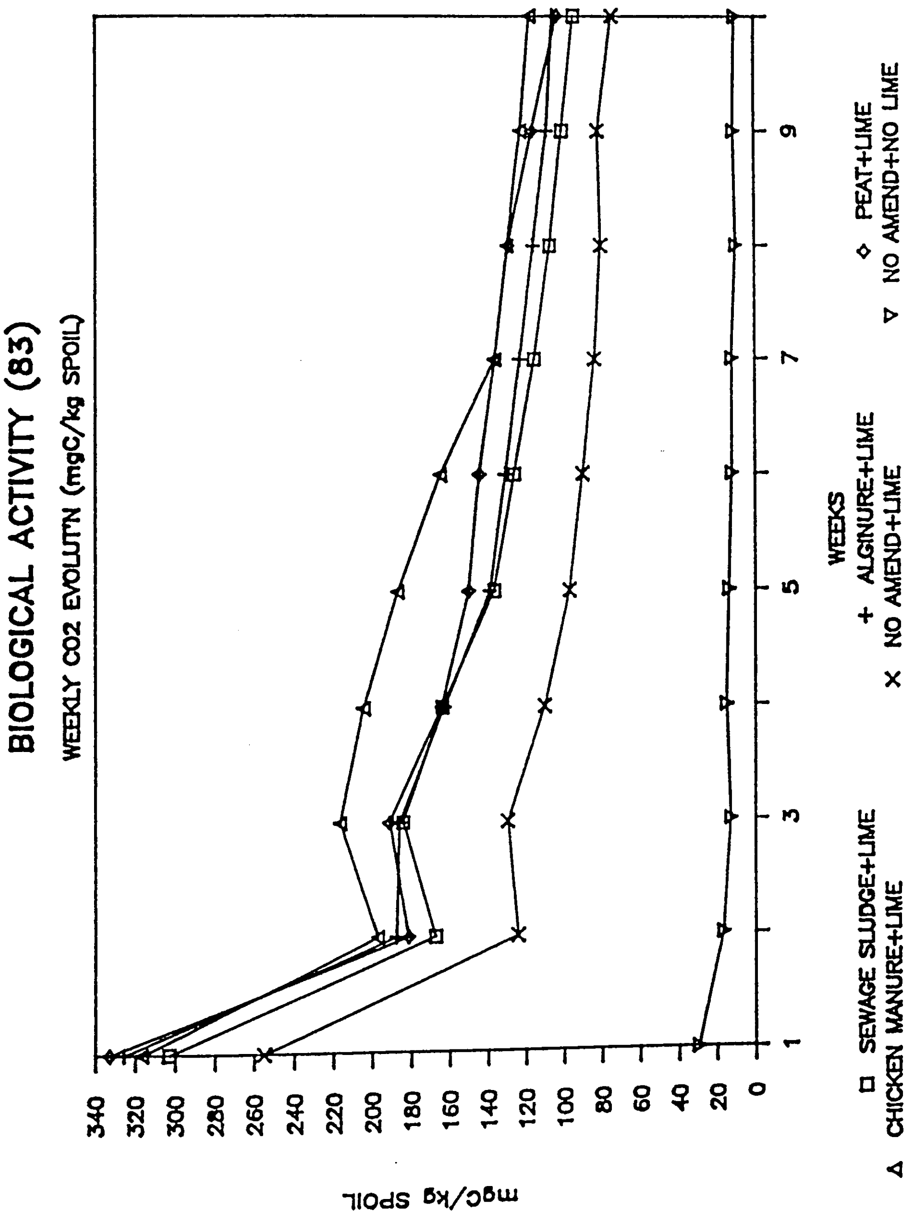
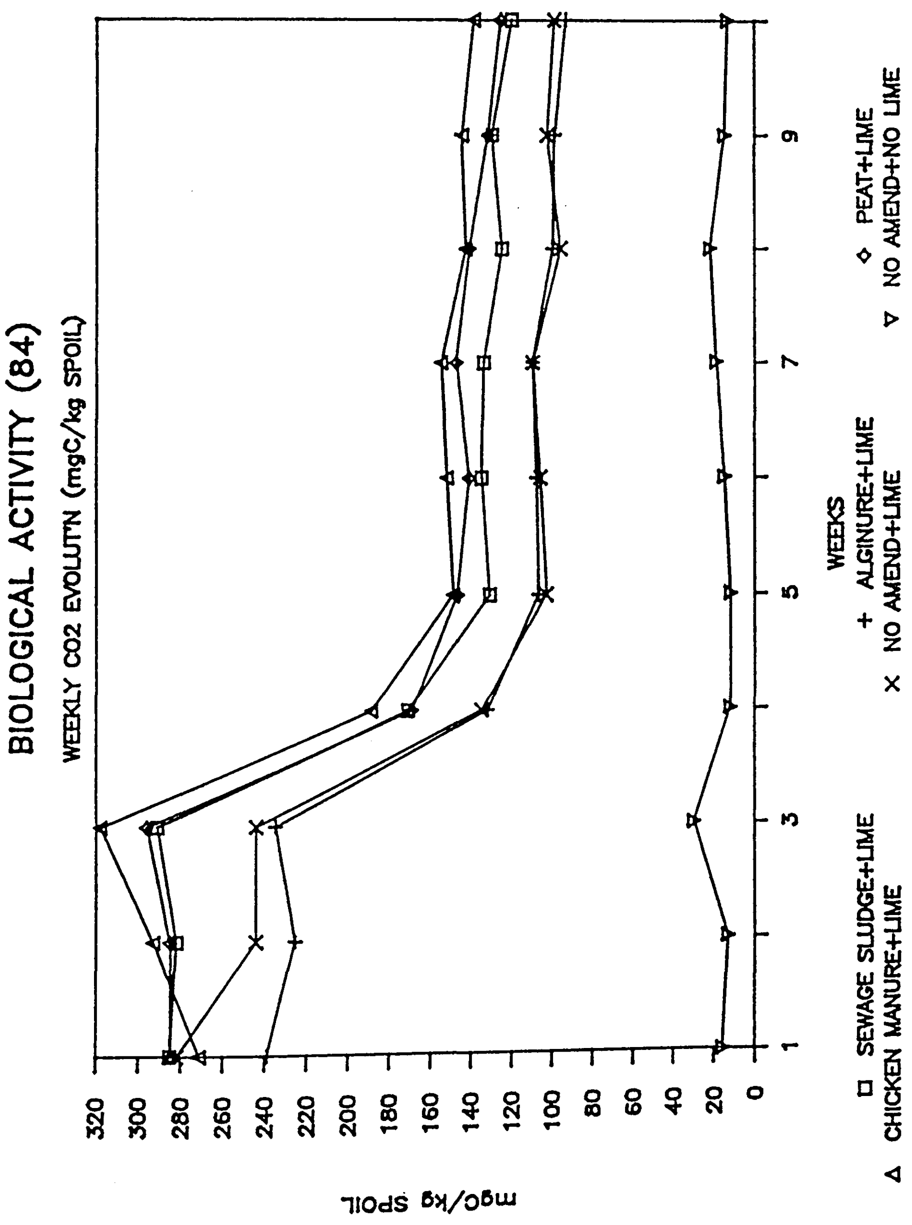

BIOLOGICAL ACTIVITY (83)
WEEKLY CO2 EVOLUT'N (mgC/kg SPOIL)
mgC/kg SPOIL
340
320
300
280
260
240
220
200
180
160
140
120
100
80
60
40
20
0
1
3
5
7
9
WEEKS
□ SEWAGE SLUDGE+LIME
+ ALGINURE+LIME
◇ PEAT+LIME
△ CHICKEN MANURE+LIME
× NO AMEND+LIME
▽ NO AMEND+NO LIME

Figure 3.4


BIOLOGICAL ACTIVITY (84)
WEEKLY CO2 EVOLUTN (mgC/kg SPOIL)
mgC/kg SPOIL
320
300
280
260
240
220
200
180
160
140
120
100
80
60
40
20
0
1
3
5
7
9
WEEKS
□ SEWAGE SLUDGE+LIME
+ ALGINURE+LIME
◇ PEAT+LIME
△ CHICKEN MANURE+LIME
× NO AMEND+LIME
▽ NO AMEND+NO LIME

The limed samples taken in 1983 evolved between 1,100 and 1,800 mg/kg CO_2-C compared to 1,400 - 1,950 for the corresponding samples taken in 1984. The order of treatments in 1983 was Chicken Manure + Lime > Peat + Lime > Alginure + Lime > Sewage Sludge + Lime > Lime. This sequence was maintained in the 1984 samples apart from the alginure and lime treatment which evolved less CO_2 than the lime only treatment. Although the values obtained over the two years indicated a certain order of merit in organic matter decomposition levels between the treatments, when the three areas were looked at separately this was not found. The total CO_2-C evolved for each treatment in all three areas for the years 1983 and 1984 are shown in Tables 3.12 and 3.13 respectively. There was no consistency in the order of evolution between the three areas, or even in the one area from the first year to the second. The plots that received no lime and no amendment showed very low levels of organic matter decomposition which is consistent with the fact that there was no source of humified organic matter within these plots. The low pH in these untreated spoils may have also contributed to the lack of microbial activity, however this had no apparent adverse effect on the alginure + lime plot in area C, 1983.

Table 3.12 Total CO_2 evolution in mg C/kg (1983)

AREA	TREATMENT					
	Sewage Sludge + Lime	Alginure + Lime	Peat + Lime	Chicken Manure + Lime	Lime	Control
A	1737.5	1629.3	1612.5	1861.8	769.0	111.9
B	1372.0	1696.3	1629.1	1621.0	1696.3	155.7
C	1392.7	1433.4	1707.6	1902.3	917.7	160.1

Table 3.13 Total CO_2 evolution in mg C/kg (1984)

	TREATMENT					
AREA	Sewage Sludge + Lime	Alginure + Lime	Peat + Lime	Chicken Manure + Lime	Lime	Control
A	221.0	1669.6	729.8	1725.2	1273.8	121.8
B	1448.4	1630.4	2415.8	1414.0	1759.6	148.8
C	1756.8	1047.2	2461.8	2724.4	1534.2	219.2

The higher levels of carbon dioxide evolved in the majority of the 1984 samples compared to the corresponding samples in 1983 can be explained by the extended microbial flush in activity observed for that experiment (Figures 3.3 and 3.4). A possible explanation for this was that during the latter experiment subsamples were removed for a mineralisation study. Although this was carried out with care it was impossible not to disturb the incubating material slightly, and this would have had the greatest effect during the first two weeks when the microbial population was highly active. The spoils appeared to have reached a steady state decomposition rate by week five and these lay in the range 80-140 mg CO_2-C/kg/week for the limed treatments. The untreated spoil gave $\sim$20 mg CO_2-C/kg /week. These respiration rates varied between areas in the same manner as the total evolution of carbon dioxide so it was impossible to identify one treatment as being better than the rest. The evidence from both the total cumulative carbon dioxide evolution and the basal respiration rates from both years (Figures 3.1-3.4) suggest that there was little if any enhancement of microbial activity, and hence organic matter build-up, in the plots that received an organic amendment. This could be explained by the fact that the majority of the organic material that was incorporated into the spoil during cultivation of the treatments had been decomposed during the previous four years. The subsequent accumulation of organic matter would then rely heavily on the incorporation of the decaying vegetation. The extremely harsh chemical and physical conditions which are an integral part of coal spoil result in an environment that is hostile to mesofaunal activity which leads to a very poor incorporation of dead vegetation. In fact, during all spoil samplings, there was no evidence of an earthworm population. This poor incorporation is the same regardless of treatment with the consequence that the build-up of organic matter in the spoil was the same for all plots that had a vegetative cover resulting in similar levels of microbial activity. The poor organic incorporation led to the establishment of a litter layer on top of the spoil material, the depth of which varied with treatment. The addition of organic amendments during this reclamation study did enhance the accumulation of organic matter, but the majority of this remained on the surface with only small amounts being incorporated into the spoil. To overcome this problem and develop a more soil-like environment within the spoil, this litter layer could be manually mixed into the top 15-20 cm. However this might lead to problems of re-establishing a vegetative cover which may require additional fertilisation thus increasing maintenance costs. An alternative would be to introduce a mesofaunal population that would accelerate the incorporation of this organic layer without disturbing the established plant-soil system too drastically.

3.4 CONCLUSION

The results in Section 3.3.1 indicate that the chemical techniques developed to determine organic carbon or organic matter within a soil are of limited use when trying to detect the presence of humified organic matter in a background of black shale such as that found at Baads Colliery, West Lothian. Pederson et al. (1978) found similar problems when using loss on ignition and the Walkley-Black procedure and concluded that organic carbon in mine soils cannot be accurately determined by either of these methods when shale and coal fragments are present. Berg (1978) and Daniels and Amos (1980) also commented on the unsuitability of applying methods for measuring soil organic matter to spoils.

In contrast, Down (1975b) and Joost et al. (1987) have used the Walkley and Black method to demonstrate the build-up of organic matter with age and sewage sludge/lime treatment of coal spoil respectively. Rimmer (1982) used the difference in loss on ignition between the depths 0-5 cm and 5-30 cm to show the accumulation of organic matter with age in coal spoils. The hydrogen peroxide treatment was also used (Rimmer and Gildon 1986) to demonstrate the effect of amendments and grass species on organic matter accumulation.

It is apparent therefore that the use of chemical techniques to estimate organic matter accumulation in coal spoils is very much dependant on the nature of the coal spoil itself. The material used in this study did not lend itself to these methods.

It has been demonstrated that the numbers and diversity of micro-organisms are lower in mine soils than in native soils (Wilson 1965) and also that organic matter decomposition is slower in mine soils (Lawrey 1977). However the presence of vegetation can increase the number and activity of these micro-organisms (Wilson and Hendrich 1957; Stroo and Jenks 1982). The addition of fertilisers and organic amendments such as sewage sludge can also increase the microbial activities in minespoils (Stroo and Jenks 1985; Rimmer and Gildon 1986).

The results from this present study indicated that the most important factor involved in increasing the microbial activity within the spoil was the addition of lime, which raised the basal respiration rate from 2.8 mg CO_2-C kg^{-1} day^{-1} to 12.8 mg CO_2-C kg^{-1} day^{-1}. The use of organic amendments in the reclamation scheme further enhanced the microbial activity into the range of 15.7 -> 21.4 mg CO_2-C kg^{-1} day^{-1}. Although this increase indicates a slight accumulation of organic matter in the spoil, the majority of the dead vegetation produced was to be found lying on the surface as a distinct layer. Even though it appears that the majority of the organic matter is not being incorporated, the respiration rates are similar to those found by Rimmer and Gildon (1986) who used fertiliser, sewage sludge and straw in their reclamation scheme.

The comparison of the biological activities found in the reclaimed coal spoil to those found in soils of known organic matter content could give an indirect measurement of organic matter accumulation due to the various treatments. Table 3.14 shows the average respiration rate (mg CO_2-C kg^{-1} day^{-1}) of six soils during the 10-20 day period of a soil biomass experiment (Powlson and Jenkinson 1976). The different soils have received various treatments and so have accumulated a range of organic matter contents. When compared to the respiration rates for these soils, the respiration rates of the amended colliery plots indicate the presence of 2.8-3.5% organic carbon. Although not a direct measurement, this narrow range of organic carbon content highlights the similarity between treatments brought about by the poor incorporation of the dead plant tissue.

These experiments have shown that when the use of standard chemical techniques to measure organic content in coal spoil are ruled out due to the nature of the material, microbial respiration rates can be employed to compare the effect of different reclamation techniques, and provide an indication of organic matter accumulation.

Table 3.14 Taken from Poulson and Jenkinson (1976)

Soil	% Org. C	Av. mg CO_2-C kg^{-1} day^{-1} for 10-20 day period
Broadbalk Continuous Wheat treated with FYM	2.81	12.2
Broadbalk Continuous Wheat no manure	0.93	6.4
Broadbalk Wilderness under woodland	4.3	27
Whitehores Field arable	2.73	8.9
Flint Field under grass	9.91	31.8
Geescroft Wilderness under woodland	2.95	14.8

CHAPTER 4

ACCUMULATION AND TURNOVER OF THE MACRO-NUTRIENTS N, P AND K

4.1 INTRODUCTION

In well-developed soils under a complete vegetation cover, the supply of plant macro-nutrients is maintained through biogeochemical cycles between plants and soil. The most important elements for plants are nitrogen, phosphorus and potassium. The chemical forms of these elements which are being cycled are referred to as the active pool (Chadwick 1975) while the relatively unavailable elements are present in a storage pool, either the parent material or organic matter. In colliery shales, the active pool is usually absent. Therefore it is the storage pool that is important in providing the necessary macro-nutrients for plant establishment and growth. The quantity and rate of release of macro-nutrients from this storage pool is of great importance in the early stages of plant establishment (Kent 1982).

There are considerable amounts of nitrogen, unavailable to plants, in the coal and carbonaceous shales of colliery spoil (Cornwell and Stone 1968, 1973; Aldag and Srtzyszcz 1980; Palmer, Morgan and Williams 1985), although some may be released by weathering in very acid environments (Cornwell and Stone 1968). Phosphorus is either absent or available in very low quantities in most colliery shales (Kohnke 1950; Einspahr et al. 1955; Doubleday 1970, 1972; Berg 1973; Chadwick 1973a,b; Gemmell 1973, 1977; Fitter and Bradshaw 1974).

Potassium is rarely deficient in colliery shales as it occurs in abundance in clay minerals (Kohnke 1950; Doubleday 1970, 1972; Berg 1973; Gemmell 1973).

Due to the unfavourable water and temperature relations that exist within colliery shale it is essential to get a quick establishment of vegetation with deep rooting systems. The availability of macro-nutrients has an important effect on root depth (Duncan and Ohlrogge 1958; Fitter and Bradshaw 1974).

In a natural system, the majority of the nitrogen and some of the phosphorus comes from the organic pool (Russell 1973). However, since there is no source of organic matter in colliery shales the nutrients required for establishment must come from another source. Fertilisers are usually applied to encourage growth, but this is only a short-term measure due to leaching losses, especially of nitrogen. If the site is subsequently managed, for agricultural or recreational use, the nutritional level may be maintained by further applications of fertilisers. In many cases, however, reclamation does not have a specific aim, other than cosmetic purposes, and so management ceases after the establishment period. In this case an active pool has to be built up to allow a self-sustaining ecosystem to develop (Bradshaw et al. 1975; Marrs, Roberts and Bradshaw 1980; Roberts, Marrs and Bradshaw 1980). This can either be done by the use of organic amendments (Leycher and Kunkle 1973; Berry and Marx 1977; Yam 1984; Topperand Sabey 1986), or in the case of nitrogen the use of legumes to fix nitrogen from the atmosphere (Ruffner and Hall 1963; Miles, Rubble and Bond 1973; Bennet et al. 1978). Once this active pool has been established, the supply of nutrients to plants depends on nutrient cycling via the decomposition of plant litter (Lanning and Williams 1979) and the mineralisation of the spoil organic matter (Williams and Cooper 1976; Reeder and Berg 1977; Roberts, Marrs and Bradshaw 1980).

This chapter compares the ability of four organic amendments to supply a long-term source of nitrogen, phosphorus and potassium to a limed acidic spoil. The nutrient capital was measured four and five years after initial reclamation and the contribution of spoil, litter and herbage to this capital was calculated. In addition the mineralisation of spoil organic matter accumulated from each treatment was determined. Finally the response of vegetation to maintenance additions of fertiliser N, P and K was assessed.

4.2 MATERIALS AND METHODS

4.2.1 Nutrient budgets

Experimental plots (8 m x 3 m) were set up at Baads Colliery, West Lothian in 1979. The plots used in this section received the following initial treatments; chicken manure, sewage sludge, Alginure (a seaweed-based soil conditioner), peat and no organic amendment applied to limed (25 t/ha) spoil. The unamended, unlimed plots were also used. All plots received 300 kg/ha of a 15:10:10 NPK fertiliser. In 1981 a further application of 15:10:10 fertiliser (300 kg/ha) and lime (5 t/ha) were added to one half of the 8 m x 3 m plots.

All the plots (both halves) were sampled in triplicate at the end of the growing season in 1983 and 1984.

4.2.1.1 Spoil

Triplicate spoil samples were taken to a depth of 15 cm from the experimental plots described above. These were then air-dried at room temperature and sieved to collect the < 2 mm fraction. The spoil pH was measured in a 1:2.5 spoil:water suspension using a combination pH electrode and moisture content by weight difference on heating to 110°C.

4.2.1.1.1 Extraction/filtration procedures

i) Ammonium and nitrate nitrogen.

Extractant purified 1 M potassium chloride.

The pH of the 1 M potassium chloride was raised to 11 using potassium hydroxide and the solution was then brought to the boil. This removed any possible ammonium nitrogen contamination. The solution was then allowed to cool and was finally brought back to its original pH using hydrochloric acid. Duplicate 2.5 g air-dry samples were shaken in a spoil:solution ratio of 1:20 for two hours at 4°C. The lower temperature was used to reduce any mineralisation of nitrogen during extraction. The extracts were then filtered through a Whatman's no. 40 filter paper with the first 25 ml of filtrate being discarded from the filter papers. The second 25 ml of the filtrate was collected and stored at $2^{o}C$ ready for analysis.

ii) Phosphate and potassium.

Extractant - 2.5% acetic acid.

Duplicate 2.5 g air-dry samples were shaken end over end in a spoil:solution of 1:20 for 2 hours at room temperature. This was a lower spoil:solution ratio than that commonly used by the Scottish advisory service because of the inherent low levels of available phosphate in colliery spoil. The extracts were then filtered through Whatmans no. 40 filter papers (no problem with P and K contamination) and the filtrate collected and stored at $2^{o}C$ ready for analysis.

In both cases blank extractions were run with no spoil to allow for contamination error.

4.2.1.1.2 Filtrate analysis

Ammonium-N, nitrate-N and phosphate-P were analysed colorimetrically using a Tecnicon Autoanalyser 2 System. Potassium was measured by flame emission photometry on an EEL (Evan Electroselenium Ltd.) flame photomenter.

i) Ammonium-N

Ammonium-N was determined by a modification of the indophenol green method (Brown 1973) using a complexing reagent to prevent interferences due to the precipitation of hydroxides in the reagent stream.

The calibration curve is linear over the range 0-4 mg/l ammonium-N.

Reagents - (a) Alkaline Phenol:

Phenol	50 g
NaOH	22.5 g
Deionised water	1 litre

(b) Complexing Reagent:

Potassium sodium tartrate	50 g
Sodium citrate	50 g
Sodium nitroprusside	1.2 g
30% Brij-35 solution	0.5 ml
Deionised water	1 litre

(c) Sodium Hypochlorite Solution (0.5% available chlorine)

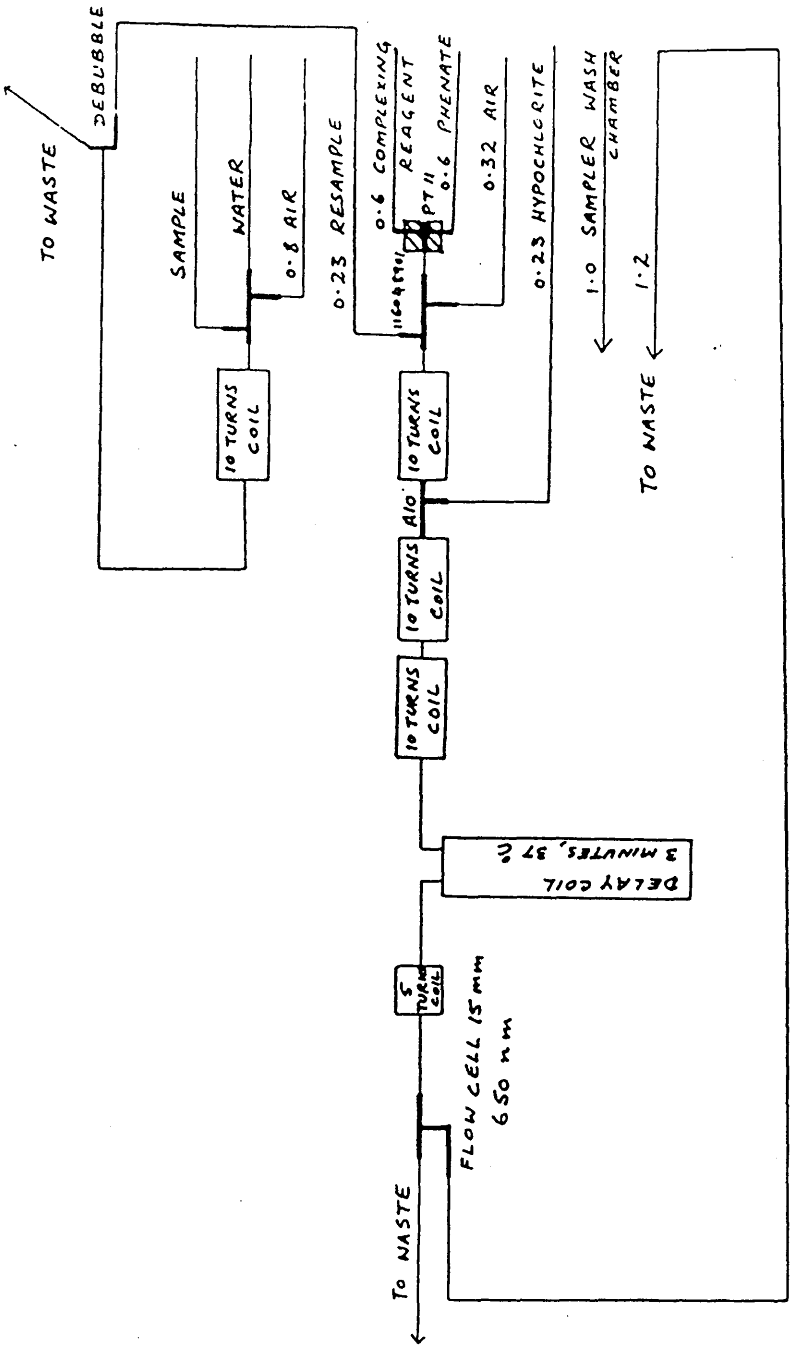
(d) Standards in the range of 0-1 mg/l ammonium-N were made up in extracting solution.

Methodology

A schematic diagram of the ammonium manifold can be found in Figure 4.1. The colour development was carried out at a constant temperature (25^{o}C) to improve stability. Colour intensity was measured at 650 nm and a sampling rate of 40 hr^{-1} was used with a sample:wash ratio of 9:1.

Figure 4.1 Technicon manifold for determining Ammonium-N by the indophenol green method

Figure 4.1


TO WASTE
DEBUBBLE
SAMPLE
WATER
0·8 AIR
10 TURNS COIL
0·23 RESAMPLE
0·6 COMPLEXING REAGENT
PT 11
0·6 PHENATE
0·32 AIR
0·23 HYPOCHLORITE
1·0 SAMPLER WASH CHAMBER
1·2
TO WASTE
116048901
10 TURNS COIL
A10
10 TURNS COIL
10 TURNS COIL
DELAY COIL 3 MINUTES, 37°C
5 TURN COIL
FLOW CELL 15 mm 650 nm
TO WASTE

ii) Nitrate-N

The method for nitrate was a modification of that outlined by Best (1976) where the nitrate is reduced to nitrite which is then determined using the Greiss reaction. The method therefore measures nitrate and nitrite, but nitrite may be determined separately on the same manifold by omitting the reduction step. The yield of nitrite from the reduction of nitrate is low and falls at higher nitrate concentrations. Thus it is essential to use dilute samples in order to obtain a linear calibration curve. The manifold can be used to determine nitrate over the ranges 0-1 mg/l up to 1-100 mg/l using a single dilution step.

Reagents - (a) Buffer Solution:

Sodium tetraborate	22.5 g
Sodium hydroxide	2.5 g
Deionised water	1 litre

(b) Greiss Reagent:

Concentrated hydrochloric acid	100 ml
Sulphanilamide	10 g
N-1-napthylethylenediamine dihydrochloride	0.5 g
Deionised water	1 litre

(c) Reducing Reagent:

Hydrazinium sulphate	0.15 g
Copper sulphate	0.015 g

30% Brij-35 solution	0.15 ml
Deionised water	1 litre

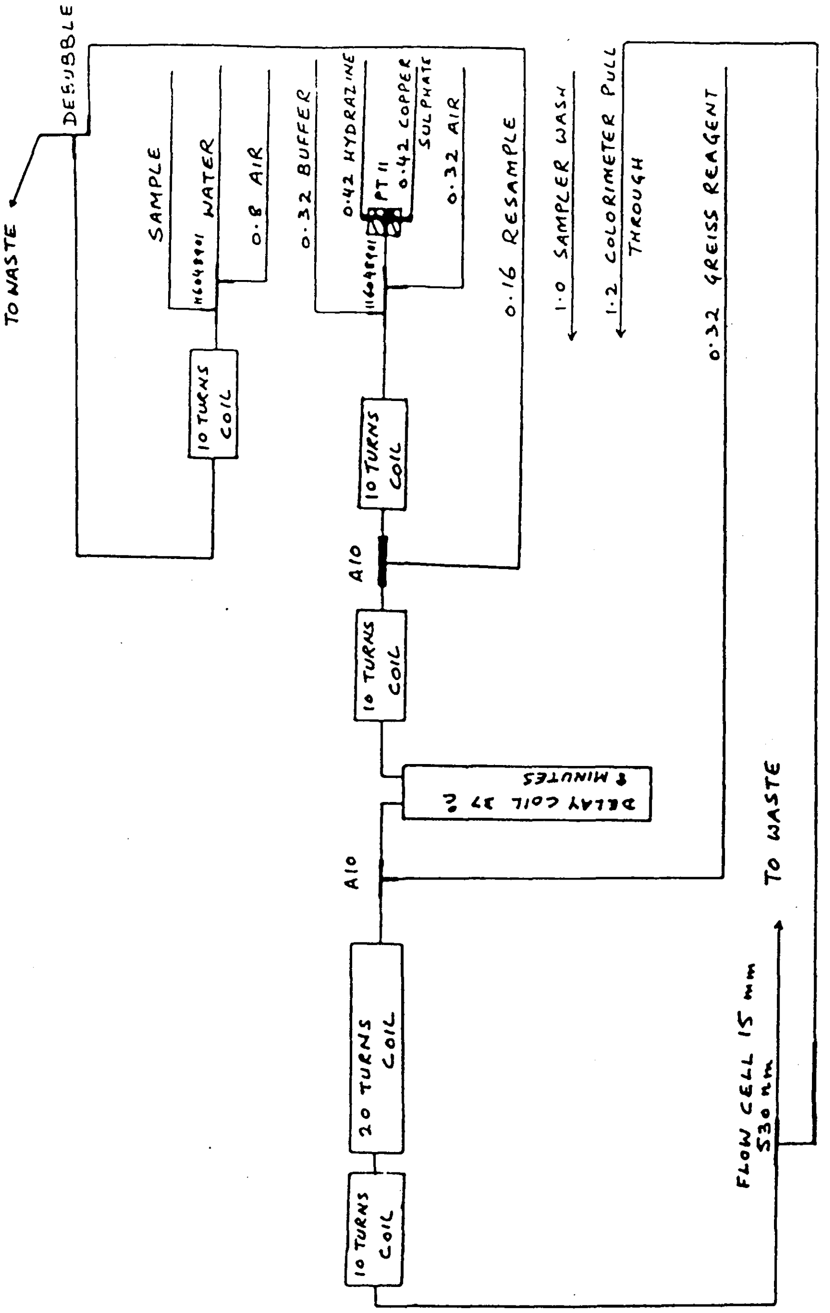
(d) Standards - range 0-1 mg/l in extractant.

Methodology

Figure 4.2 shows a schematic diagram of the nitrate manifold. The reduction step was carried out at a pH of 9.5 and at a temperature of 37°C using a G coil in a constant temperature bath. The samples were run at a rate of 40 hr^{-1} and the colour intensity measured at 530 nm.

Figure 4.2 Technicon manifold for determining Nitrate-N using the Greiss reaction

Figure 4.2


TO WASTE
DEBUBBLE
SAMPLE
WATER
0·8 AIR
0·32 BUFFER
0·42 HYDRAZINE
PT 11
0·42 COPPER SULPHATE
0·32 AIR
0·16 RESAMPLE
1·0 SAMPLER WASH
1·2 COLORIMETER PULL THROUGH
0·32 GREISS REAGENT
10 TURNS COIL
10 TURNS COIL
A10
10 TURNS COIL
DELAY COIL 37 °C 8 MINUTES
A10
20 TURNS COIL
10 TURNS COIL
FLOW CELL 15 mm 530 nm
TO WASTE

iii) Phosphate-P

The method was based on the formation of a phospho-molybdenum complex which was reduced using ascorbic acid to give a blue colour which may be measured at 660 or 880 nm.

Reagents - (a) Acid Molybdate:

Ammonium molybdate	5.2 g
Antimony potassium tartrate	0.1 g
Conc. sulphuric acid	60 ml
Deionised water	1 litre

The antimony potssium tartrate must be dissolved in deionised water before addition to prevent precipitation.

(b) Ascorbic Acid:

Ascorbic acid	0.75 g
Deionised water	100 ml

This reagent was made up fresh every day.

(c) Wetting Agent:

Aerosol-22 (30% soln.)	1 ml
Deionised water	1 litre

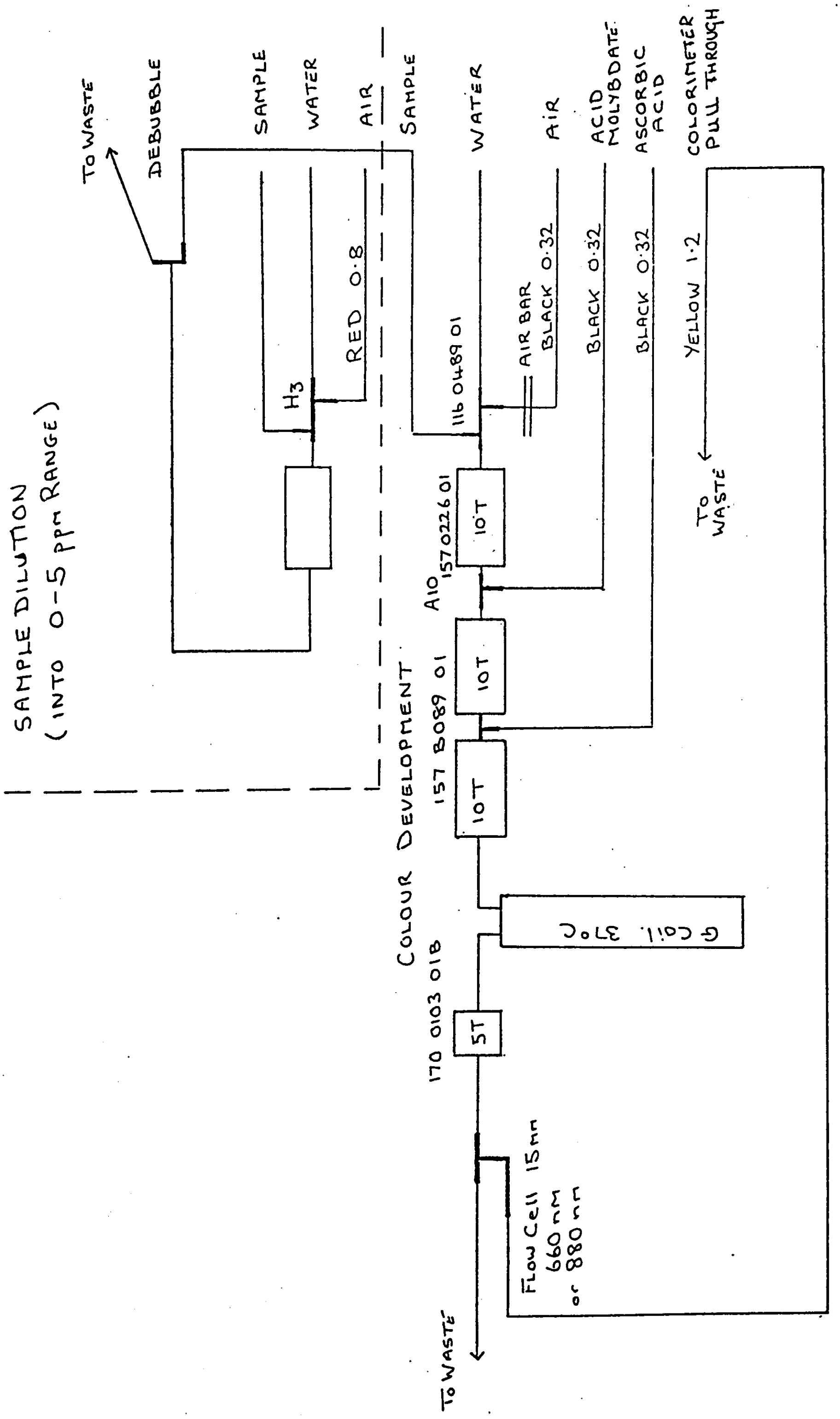
(d) Standards in the range 0-5 mg/l phosphate-P made up in extracting solution.

Methodology

A schematic diagram of the phosphate manifold using acid molybdate is shown in Figure 4.3. The system gives a linear response up to a maximum of 0.8 mg/l-P in the reagent stream, but ideally a maximum of 0.05 mg/l-P should be used. The sample and water flow rates can be arranged to enable samples up to a concentration of 5 mg/l-P to be used provided the flow rate of samples and water is approximately 1 ml min^{-1}. Samples were normally run at fifty per hour, but when a separate dilution step was required this was reduced to forty per hour. The absorbance peak at 660 nm was used to detect the molybdenum blue complex.

Figure 4.3 Technicon manifold for determining Phosphate-P using the molybdenum blue method

Figure 4.3


SAMPLE DILUTION
(INTO 0-5 ppm RANGE)
TO WASTE
DEBUBBLE
SAMPLE
WATER
AIR
RED 0·8
H3
SAMPLE
WATER
AIR
ACID MOLYBDATE
ASCORBIC ACID
COLORIMETER PULL THROUGH
116 0489 01
AIR BAR
BLACK 0·32
BLACK 0·32
BLACK 0·32
YELLOW 1·2
TO WASTE
157 0226 01
A10
10T
157 B089 01
10T
10T
COLOUR DEVELOPMENT
G Coil 37°C
170 0103 01B
5T
Flow Cell 15mm
660nm
or 880nm
TO WASTE

iv) Potassium

The potassium concentrations of the spoil extracts were measured directly by flame emission spectrophotometry. Standards in the range 0-10 mg/l K were prepared using the extractant solution (2.5% acetic acid) and with these a standard curve was drawn up using the 0-100% deflectance range on the flame photometer. The deflectance reading of the samples was measured and the concentration calculated from the standard graph.

4.2.1.2 Herbage

A 0.25 m^2 quadrat was used to take triplicate vegetation samples from the plots described in Section 4.2.1. The herbage was clipped to a height of approximately 3 cm and the samples collected in polythene bags. The fresh weight yeild was measured on return to the laboratory and the samples were then transferred to the oven at 110°C for 48 hours. After the oven-dry yield was measured a representative subsample was milled and the material passing through a 2 mm sieve was collected for analysis.

4.2.1.2.1 Digestion procedure

The digestion procedure used was based on the micro-Kjeldahl method of Bremner (1960). The digestion was carried out in 50 ml pyrex Kjeldahl flasks on a gas heated digestion stand. Enough sample was used to give approximately 10 mg ammonium-N (0.4 g of herbage) and to this a 1 g tablet of Na_2SO_4:Se (100:5) was added as a catalyst. A sodium salt was used in the catalyst in preference to potassium as the digest was to be analysed for potassium. A further 1 g of Na_2SO_4 was added to raise the boiling temperature of the digestion mixture. Five millilitres of concentrated H_2SO_4 were added prior to placing the flasks on the digestion rack. The samples were heated gently at first, then more strongly until the digest had cleared. Heating was continued, with the acid condensing one third of the way up the flask, for a further 5 hours after clearing. The digest mixture was allowed to cool and was then diluted with approximately 50 ml of deionised water. This solution was then quantitatively transferred to a 100 ml volumetric flask through a Whatmans no. 40 filter paper. The flask was made up to the mark with deionised water and the samples were ready for analysis.

4.2.1.2.2 Analysis

Ammonium-N and Phosphate-P were analysed colorometrically using a Tecnicon Autoanalyser 2 System, potassium by flame emission photometry on an EEL (Evan Electroselenium Ltd) flame photometer.

i) Ammonium-N

The determination of ammonium-N in acid digests was made by further modifying the indophenol green method described in Section 4.2.1.1.2 i).

Reagents - In addition to the usual reagents the following are also required:

Wash chamber solution	5% H_2SO_4

Neutralising solution	3.6 g NaOH per litre
Methyl Red indicator	0.1% solution in water
Molar NaOH	

All standards were made up from a solution containing the same concentration of acid and catalyst mixture as the final sample solutions.

Methodology

The standard ammonium-N manifold (Figure 4.1) was used with the following modifications:

(a) Sampler wash solution - 5% v/v H_2SO_4

(b) Dilution step - ratio 20:1

Sample	0.1 ml min^{-1}
Diluent	2.0 ml min^{-1}
Air	0.8 ml min^{-1}

The concentration of the dilutent neutralising solution was checked by sampling a portion of the wash chamber solution containing a few drops of methyl red indicator. If required, some M NaOH was added to the neutralising solution until the indicator just changes colour from red to yellow in the dilution mixing coil.

(c) The alkaline phenol and complexing reagent were mixed a few hours prior to analysis. This reduced the sensitivity of the system and allowed analysis of concentrations in the range up to 100 mg/l ammonium-N. Both reagent lines were placed in this solution.

A sampling rate of 40 per hour was used.

ii) Phosphate-P

Phosphate-P in acid digests containing selenium could not be determined using the ascorbic acid/molybdenum blue method. However, by the formation of a yellow phospho-vanado-molybdate complex which absorbs at 420 nm, phosphate was determined in these digests. Determination was linear in the range 0-50 mg/l phosphate-P.

Reagents

(a) Ammonium molybdate/Ammonium metavanadate:

Ammonium molybdate	25 g
Ammonium metavanadate	1.25 g
Levor IV	1 ml
Deionised water	1 litre

(b) Nitric acid 0.8M (0.25M for acid digest)

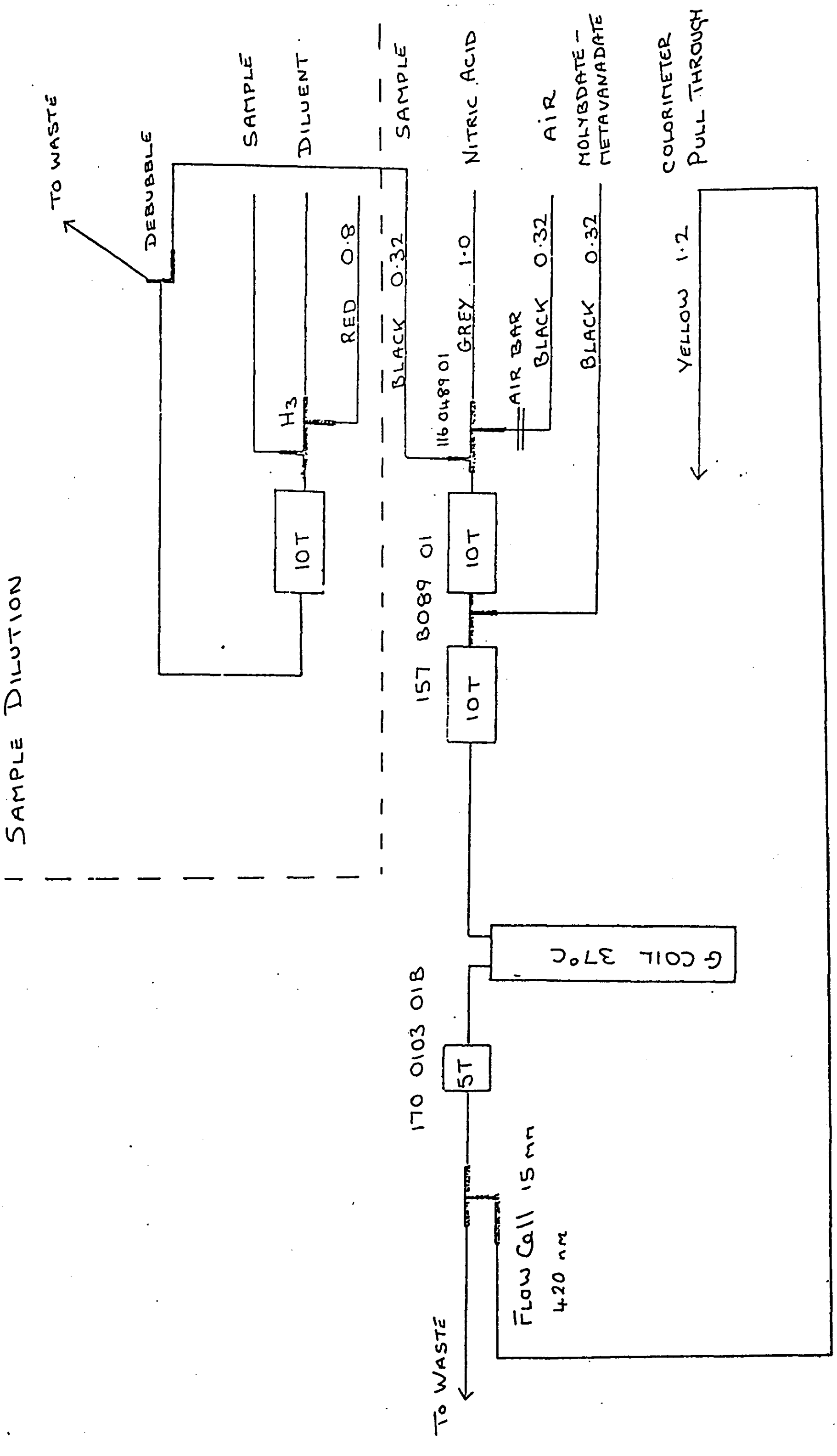
(c) Standards in the range 0-10 mg/l phosphate-P were made up using a solution containing the same acid and catalyst concentrations as the samples.

Methodology

The phospho-vanado-molybdate manifold is shown in Figure 4.4. A sampling rate of 40 per hour was used and the subsequent coloured complex determined at 420 nm.

Figure 4.4 Technicon manifold for determining Phosphate-P using the vanado-molybdate method

Figure 4.4


SAMPLE DILUTION
TO WASTE
DEBUBBLE
SAMPLE
DILUENT
RED 0·8
H3
10T
SAMPLE
NITRIC ACID
AIR
MOLYBDATE-METAVANADATE
COLORIMETER PULL THROUGH
BLACK 0·32
GREY 1·0
AIR BAR
BLACK 0·32
BLACK 0·32
YELLOW 1·2
116 0489 01
157 8089 01
10T
10T
G COIL 37°C
170 0103 01B
5T
Flow Cell 15 mm
420 nm
TO WASTE

iii) Potassium

A subsample of the acid digests were diluted one in twenty with deionised water prior to potassium determination. This brought the sample concentrations down into the range of 0-5 mg/l K that was used to prepare the standard curve. All standards were prepared using a solution of similar acid and catalyst concentrations to the diluted samples. Both standards and samples were analysed for potassium by flame emission spectophotometry using the deflectance range of 0-100%.

4.2.1.3 Litter layer

Triplicate cores were taken from the plots described in Section 4.2.1. These were air-dried in the laboratory and the litter layer removed. This was then separated into two fractions by way of a 2 mm sieve. The fraction that failed to pass through the sieve was thought to represent the undecomposed and partially decomposed herbage and root material. The <2mm fraction would then correspond to the further decomposed and humified material. The latter fraction was separated from any associated spoil material by flotation in water. Both fractions were then oven-dried at 110^{o}C for forty eight hours and the oven-dry yield measured. The greater than 2 mm fraction was then milled in a blender to pass through a 2 mm sieve. Both fractions were then digested and analysed by the methods described for herbage in Section 4.2.1.2.

4.2.2 Phosphate adsorption

Two samples of black colliery spoil were taken from Baads Colliery, West Lothian, one unlimed, the other having received lime at the rate of 25 tonnes per hectare. Both samples were air-dried at room temperature and sieved to collect the less than 2 mm fraction. Spoil pH was measured in a 1:2.5 spoil:water suspension using a combination pH electrode, and moisture content by weight difference on heating to 110°C for forty eight hours.

Phosphate adsorption isotherms were determined by equilibrating 100 ml of solutions containing 1, 2, 5, 10, 15, 20, 30, 40, 50, 60, 70, 80, 90 and 100 mg/l phosphate-P (from $CaH_4(PO_4)_2.H_2O$) with 5 g air-dried spoil for 18 hours. The samples were then filtered through Whatman's no. 40 filter papers and collected for analysis. The filter papers had previously been checked for any phosphate contamination or adsorption ability. Phosphate-P in solution was determined by the molybdenum blue colorometric technique described in Section 4.2.1.1.2 iii).

The amount of phosphate adsorbed by the spoil was calculated from the difference between the original and equilibrium solution concentrations.

4.2.3 Potassium relationships in spoil

Samples from the two spoils, Baads limed and unlimed, described in Section 4.2.2 were used in this investigation.

4.2.3.1 Quantity/intensity

One 0.5 g and seven 5 g samples of air-dried spoil were weighed out in duplicate. To these 50 ml of the following solutions containing increasing potassium concentrations in 0.01 M $CaCl_2$ were added.

Wt. spoil	Potassium conc.
0.5 g	0 mM K in 0.01M $CaCl_2$
5 g	0 mM K " " "
5 g	0.1 mM K " " "
5 g	0.5 mM K " " "
5 g	1 mM K " " "
5 g	2 mM K " " "
5 g	3 mM K " " "
5 g	5 mM K " " "

These were then shaken end over end for thirty minutes and filtered through a Whatmans no. 40 filter paper. The final K equilibrium concentration was determined by flame photometry as in Section 4.2.1.1.2 iv). Standards were made up to cover two ranges due to the wide differences in equilibrium K concentrations. These were 0-1 mM K in 0.01 M $CaCl_2$ and 0-5 mM K in 0.01 M $CaCl_2$.

4.2.3.2 Desorption curve

To six 1 g samples of spoil, 10 ml of 5 mM K in 0.01 M $CaCl_2$ were added. These were shaken end over end for thirty minutes and then the following volumes of 0 mM K in 0.01 M $CaCl_2$ were added.

0 ml 0 mM K in 0.01 M $CaCl_2$
10 ml " " " " " " "
25 ml " " " " " " "
50 ml " " " " " " "
100 ml " " " " " " "
200 ml " " " " " " "

These were shaken for a further thirty minutes and then filtered through a Whatmans no. 40 filter paper. The final potassium concentrations were measured by flame photometry as in Section 4.2.3.1.

4.2.3.3 Two hour equilibrium

Sections 4.2.3.1 and 4.2.3.2 were repeated using a two hour shake to replace the thirty minute shake in order to enable the spoil and solution mixture to obtain equilibrium.

4.2.4 Mineralisation study

Experiments to determine the levels of mineralisable nitrogen, phosphorus and potassium were run in conjunction with the microbial activity incubations described in Section 3.2.2. The extraction, filtration and analysis of nitrate-N, ammonium-N, phosphate-P and potassium were as described in Sections 4.2.1.1.1 and 4.2.1.1.2.

Prior to the incubations in both years, the initial levels of nitrate-N, ammonium-N, phosphate-P and potassium were measured by extracting duplicate 2.5 g samples of less than 4 mm material, at a moisture content equivalent to -0.5 bar soil water potential, from each treatment.

These incubations were carried out as in Section 3.2.2. In the first study, samples collected in 1983, the total levels of nutrients mineralised were measured by extracting duplicate 2.5 g samples from each treatment at the end of the ten week incubation. The quantity mineralised was calculated by difference, the final value minus the initial value.

In the second study, samples collectd in 1984, duplicate 2.5 g portions were removed, with the minimum of disturbance, during the incubation at the end of weeks 1, 2, 4, 6, 8 and 10. These subsamples were returned to the moisture content equivalent to -0.5 bar soil moisture potential.

This enabled the amount of each element mineralised to be traced through the ten week incubation and also gave the opportunity to measure rates of mineralisation for the three elements for comparison with carbon turnover.

4.2.5 Fertiliser response

Plots were established at Baads Colliery to determine the response of the vegetation to maintenance additions of nitrogen, phosphorus and potassium.

Nitrogen was applied at 50 and 100 kg N/ha using ammonium nitrate (NH_4NO_3), phosphate at 30 and 60 kg P/ha using sodium dihydrogen phosphate (NaH_2PO_4) and potassium at 50 and 60 K kg/ha using potassium chloride (KCl). These treatments were applied separately, and in combination as 50:30:30 and 100:60:60 N:P:K.

Triplicate plots (1 m^3) of each treatment and 3 controls were set up in the June of 1984 with the grass being cropped to 5 cm before fertiliser application. The subsequent growth was harvested at the end of September. Grass yield was determined and its nutrient composition measured as in Section 4.2.1.2.

4.3 RESULTS

4.3.1 Initial nutrient additions

In order to determine whether the treatments used in this reclamation study had been able to develop a self-sustaining vegetative cover, it was essential to know what levels of nutrients were applied to the coal spoil. Using these figures it was possible to ascertain how much, if any, of the major nutrients, nitrogen, phosphorus and potassium had been lost. If the levels of nutrients within the system are falling then the reclamation scheme will eventually fail if no maintenance programme is established. For this purpose samples of four organic amendments used were analysed for their nitrogen, phosphorus and potassium content.

An initial application of 15:10:10 N:P:K fertiliser at a rate of 300 kg ha^{-1} supplied 45 kg of nitrogen, 13.1 kg of phosporus and 24.9 kg of potassium per hectare to stimulate and aid in seedling development.

Chicken manure was applied at a rate of 4 t/ha with a moisture content of 14%. Analysis of the dried material produced total nutrient levels of 4.35% nitrogen, 2.43% phosphorus and 2.71% potassium.

Sewage sludge of 40% moisture was applied at 20 t/ha, and contained 0.9% N, 0.26% P and 0.16% K on a dry weight basis.

Peat was applied at a rate of 20 t/ha and had a moisture content of 60%. Analysis of the dried material produced levels of 0.22 % nitrogen, 0.06% phosphorus and 0.27% potassium.

Alginure was applied at 10.64 t.ha, but had negligible major nutrient content.

In 1981 (one year after establishment), the plots were split into two, with one half receiving a maintenance addition of inorganic fertiliser which consisted of 300 kg/ha 15:10:10 N:P:K, which supplied a further 45 kg of nitrogen, 13.1 kg of phosphorus and 24.9 kg of potassium per hectare.

The total levels of the major nutrients supplied by each experimental technique can be found in Table 4.1-4.4. Of the four organic amendments, only chicken manure and sewage sludge supplied significant amounts of nitrogen, 150 and 108 kg/ha respectively. The proportion of this initially available was approximately 60% for chicken manure and 30-40% for the sewage sludge, with the remainder becoming available over a longer time scale. Only the chicken manure supplied a reasonable quantity of phosphorus, 34 kg/ha compared to the 16 and 5 kg/ha from the sewage sludge and peat respectively. The same applies to potassium, but the peat supplied more than the sewage sludge, 22 versus 10 kg/ha.

Using these figures it was possible to determine to what extent each of the three major nutrients has been lost from the system four and five years after reclamation had been initiated.

Table 4.1 N, P and K inputs to chicken manure treated plots

ADDITION	NITROGEN kg/ha		PHOSPHORUS kg/ha		POTASSIUM kg/ha	
	A	B	A	B	A	B
Initial Fertiliser	45.0	45.0	13.1	13.1	24.9	24.9
Amendment	149.6	149.6	83.6	83.6	93.2	93.2
Maintenance Fertiliser	-	45.0	-	13.1	-	24.9
TOTAL	194.6	239.6	96.7	109.8	118.1	143.0

A - No maintenance B - Maintenance

Table 4.2 N, P and K treatments to sewage sludge treated plots

ADDITION	NITROGEN kg/ha		PHOSPHORUS kg/ha		POTASSIUM kg/ha	
	A	B	A	B	A	B
Initial Fertiliser	45.0	45.0	13.1	13.1	24.9	24.9
Amendment	108.0	108.0	31.2	31.2	19.2	19.2
Maintenance Fertiliser	-	45.0	-	13.1	-	24.9
TOTAL	153.0	198.0	44.3	57.4	44.1	69.0

A - No maintenance B - Maintenance

Table 4.3 N, P and K inputs to peat treated plots

ADDITION	NITROGEN kg/ha		PHOSPHORUS kg/ha		POTASSIUM kg/ha	
	A	B	A	B	A	B
Initial Fertiliser	45.0	45.0	13.1	13.1	24.9	24.9
Amendment	17.6	17.6	4.8	4.8	21.6	21.6
Maintenance Fertiliser	-	45.0	-	13.1	-	24.9
TOTAL	62.6	107.6	17.9	31.0	46.5	71.4

A - No maintenance B - Maintenance

Table 4.4 N, P, and K inputs to Alginure, no amendment + lime and no amendment + no lime treated plots

ADDITION	NITROGEN kg/ha		PHOSPHORUS kg/ha		POTASSIUM kg/ha	
	A	B	A	B	A	B
Initial Fertiliser	45.0	45.0	13.1	13.1	24.9	24.9
Amendment	-	-	-	-	-	-
Maintenance Fertiliser	-	45.0	-	13.1	-	24.9
TOTAL	45.0	90.0	13.1	26.2	24.9	49.8

A - No maintenance B - Maintenance

4.3.2 Levels in the spoil

4.3.2.1 Nitrogen

Unreclaimed colliery spoil has little or no nitrogen available for plant uptake. In extreme acid conditions some chemical weathering of the carbonaceous material can release nitrogen in an available form, but the extreme acidity tends to prevent plant establishment. Nitrogen in the form of fertilisers or amendments has to be applied to provide adequate levels for plant establishment and growth. Available forms of nitrogen in spoil and spoil solution are not easily quantified by chemical means, however an idea of the levels of available nitrogen in the spoil was essential to enable the determination of the total amount of nitrogen left in the reclaimed system. For this reason an extraction procedure using 1 M potassium chloride was employed to determine the levels of ammonium and nitrate in the spoil solution. These analyses were carried out at the end of the growing season four and five years after reclamation, on samples from the original plots and also those which had received a maintenance addition of lime and fertiliser. The results for extractable ammonium, nitrate and the sum of the two can be found in Tables 4.5-4.10.

Table 4.5 <u>KCl extractable ammonium (mg N/kg) in spoil (1983)</u>

TREATMENT		NO MAINTENANCE	MAINTENANCE
Chicken Manure + Lime	* **	1.15 (1.50), 1.67 (1.49), 1.58 (2.10) 1.46 (0.28)	0.26 (0.46), 6.30 (5.00), 2.16 (2.60) 2.90 (3.08)
Sewage Sludge + Lime		0.33 (0.49), 0.86 (0.96), 1.50 (0.00) 0.89 (0.58)	5.50 (5.00), 3.86 (3.50), 3.30 (3.82) 4.20 (1.14)
Alginure + Lime		2.33 (2.87), 0.60 (0.87), 0.66 (0.65) 1.20 (0.98)	4.50 (3.05), 0.97 (0.95), 7.20 (6.53) 4.22 (3.12)
Peat + Lime		3.10 (1.48), 0.27 (0.46), 2.13 (0.86) 1.83 (1.44)	2.85 (2.40), 4.70 (0.96), 6.43 (6.65) 4.66 (1.79)
No amendment + Lime		0.17 (0.29), 2.73 (2.37), 6.00 (2.85) 2.97 (2.90)	4.30 (1.67), 5.33 (1.59), 3.70 (1.64) 4.44 (0.82)
No amendment + No Lime		3.86 (2.85), 6.60 (0.50), 2.53 (2.52) 4.33 (2.07)	14.90 (1.71), 9.97 (2.37), 9.37 (1.38) 11.42 (3.03)

* Mean and standard deviations for triplicate samples from each of areas A, B and C.

** Mean and standard deviation of mean values for the three areas.

Table 4.6 KCl extractable nitrate (mg N/kg) in spoil (1983)

TREATMENT		NO MAINTENANCE	MAINTENANCE
Chicken Manure + Lime	* **	3.10 (0.65), 4.70 (0.62), 4.40 (0.62) 3.99 (0.85)	3.80 (5.20), 5.20 (0.61), 5.37 (0.47) 4.79 (0.86)
Sewage Sludge + Lime		4.47 (0.73), 4.90 (1.00), 5.43 (0.51) 4.93 (0.48)	4.90 (0.82), 4.80 (0.46), 6.13 (0.66) 5.28 (0.74)
Alginure + Lime		5.70 (0.87), 4.56 (0.35), 3.96 (0.38) 4.74 (0.88)	3.06 (0.32), 4.66 (1.07), 3.93 (1.02) 3.88 (0.80)
Peat + Lime		3.47 (0.64), 5.96 (0.38), 4.43 (2.50) 4.62 (1.25)	3.56 (0.21), 4.00 (1.34), 5.10 (1.12) 4.22 (0.79)
No amendment + Lime		4.23 (0.15), 6.07 (0.35), 6.00 (4.30) 5.43 (1.04)	3.86 (0.41), 5.70 (1.55), 6.33 (0.21) 5.30 (1.28)
No amendment + No Lime		5.46 (0.58), 6.63 (0.83), 7.36 (0.80) 6.49 (0.96)	4.76 (0.65), 9.50 (2.55), 4.53 (0.50) 6.26 (2.80)

* Mean and standard deviations for triplicate samples from each of areas A, B and C.

** Mean and standard deviation of mean values for the three areas.

Table 4.7 KCl extractable ammonium (mg N/kg) in spoil (1984)

TREATMENT	NO MAINTENANCE	MAINTENANCE
Chicken Manure * + Lime **	0.68 (0.65), 2.47 (2.20), 1.10 (1.00) 1.43 (0.94)	4.65 (3.89), 0.97 (0.87), 4.40 (2.03) 3.34 (2.05)
Sewage Sludge + Lime	0.60 (0.95), 1.63 (1.43), 4.75 (8.01) 2.33 (2.16)	8.27 (2.50), 1.57 (2.20), 11.67 (5.67) 7.18 (5.14)
Alginure + Lime	0.40 (0.10), 1.47 (1.27), 4.37 (3.92) 2.07 (2.05)	5.33 (4.50), 3.37 (4.96), 5.96 (4.94) 4.89 (1.35)
Peat + Lime	3.96 (3.59), 1.73 (1.50), 4.23 (3.41) 3.31 (1.37)	1.43 (0.51), 2.10 (0.70), 4.17 (3.81) 2.56 (1.43)
No amendment + Lime	1.93 (2.68), 1.67 (1.46), 5.40 (4.63) 3.00 (2.08)	6.07 (3.43), 4.60 (2.51), 10.20 (3.57) 6.95 (2.90)
No amendment + No Lime	15.07 (3.74), 15.70 (1.27), 12.03 (3.58) 14.26 (1.96)	7.23 (2.34), 9.07 (2.45), 11.00 (3.00) 9.10 (1.88)

* Mean and standard deviations for triplicate samples from each of areas A, B and C.

** Mean and standard deviation of mean values for the three areas.

Table 4.8 KCl extractable nitrate (mg N/kg) in spoil (1984)

TREATMENT	NO MAINTENANCE	MAINTENANCE
Chicken Manure * + Lime **	0.40 (0.69), 1.13 (0.65), 0.73 (0.25) 0.75 (0.36)	2.95 (2.30), 2.43 (3.29), 4.40 (6.08) 3.26 (1.02)
Sewage Sludge + Lime	0.76 (0.58), 0.47 (0.32), 0.43 (0.15) 0.55 (0.18)	3.73 (2.51), 0.37 (0.10), 1.45 (1.06) 1.85 (1.71)
Alginure + Lime	1.30 (2.25), 0.93 (0.32), 2.26 (3.40) 1.49 (0.68)	3.87 (3.13), 0.87 (0.89), 3.10 (3.00) 2.61 (1.56)
Peat + Lime	0.50 (0.78), 0.33 (0.21), 1.83 (0.61) 0.88 (0.82)	0.17 (0.21), 0.30 (0.14), 2.00 (2.68) 0.82 (1.02)
No amendment + Lime	0.07 (0.06), 0.73 (0.40), 1.20 (0.96) 0.66 (0.56)	0.36 (0.46), 0.20 (0.10), 1.80 (0.34) 0.79 (0.88)
No amendment + No Lime	1.20 (0.14), 1.86 (0.25), 1.60 (0.17) 1.55 (0.33)	1.16 (0.30), 1.27 (0.32), 1.67 (0.15) 1.36 (0.27)

* Mean and standard deviations for triplicate samples from each of areas A, B and C.

** Mean and standard deviation of mean values for the three areas.

Table 4.9 KCl-extractable Spoil N (mg N/kg) 1983

		No maintenance	Maintenance
Chicken Manure + Lime	NH_4-N	1.46	2.90
	NO_3-N	3.99	4.79
	TOT-N	5.45	7.69
Sewage Sludge + Lime	NH_4-N	0.89	4.20
	NO_3-N	4.93	5.28
	TOT-N	5.82	9.48
Alginure + Lime	NH_4-N	1.20	4.22
	NO_3-N	4.74	3.88
	TOT-N	5.94	8.10
Peat + Lime	NH_4-N	1.83	4.66
	NO_3-N	4.62	4.22
	TOT-N	6.45	8.88
No Amendment + Lime	NH_4-N	2.97	4.44
	NO_3-N	5.43	5.30
	TOT-N	8.40	9.74
No Amendment + No Lime	NH_4-N	4.33	11.42
	NO_3-N	6.49	6.26
	TOT-N	10.82	17.68

Table 4.10 KCl extractable Spoil N (mg N/kg) 1984

		No maintenance	Maintenance
Chicken Manure + Lime	NH_4-N	1.43	3.34
	NO_3-N	0.75	3.26
	TOT-N	2.18	6.60
Sewage Sludge + Lime	NH_4-N	2.33	7.18
	NO_3-N	0.55	1.85
	TOT-N	2.88	9.03
Alginure + Lime	NH_4-N	2.07	4.89
	NO_3-N	1.49	2.61
	TOT-N	3.56	7.50
Peat + Lime	NH_4-N	3.31	2.56
	NO_3-N	0.88	0.82
	TOT-N	4.19	3.38
No Amendment + Lime	NH_4-N	3.00	6.95
	NO_3-N	0.66	0.79
	TOT-N	3.66	7.74
No Amendment + No Lime	NH_4-N	14.26	9.10
	NO_3-N	1.55	1.36
	TOT-N	15.81	10.46

An inherent problem when dealing with coal spoil heaps is the large degree of heterogeneity of the material that has been dumped as it may come from a wide range of different sources. In the tables of results, standard deviations are shown for samples taken from within an area, and for samples between an area. The degree of variation between areas is of a similar scale to that for samples from the same plot. This is due entirely to the nature of the material as duplicate analyses of the same sample were very close. As a result of this large variation, general trends that were observed from the results will be discussed.

Four years after reclamation there appears to be little contribution from the organic manures to the levels of inorganic nitrogen found in the spoil, as all limed treatments show similar values of extractable ammonium and nitrate. The ammonium results from both 1983 and 1984 indicated that the maintenance addition of fertiliser was still providing a small amount of available nitrogen to the growing vegetation as the levels of extractable NH_4^+-N were approximately twice those found in the original plots. The highest levels of ammonium were found in the non-amended, non-limed plots as a result of chemical weathering of the spoil material. There was no vegetation growing on these plots due to the extreme acidity so none of the ammonium would be removed except for small amounts due to leaching.

In 1983 the levels of nitrate were similar if not greater than those of ammonium. This indicates the presence of the nitrifying bacteria Nitrosomonas and Nitrobacter that are required to oxidise the ammonium. 1983 was a reasonably dry summer so the nitrate levels were able to build up without being subjected to excess leaching by rain. The concentrations of nitrate in the plots that received maintenance additions of fertiliser were similar to those of the original plots, even though they had greater levels of ammonium. This could be due to the denser vegetation on these plots removing a greater proportion of the available nitrate from the spoil. The levels of nitrate in the unamended, unlimed plots were surprisingly high considering the acidity, in which the nitrifying bacteria should not survive. This nitrate could have been produced by chemical oxidation of the ammonium present in these plots.

In 1984 the extractable ammonium results were similar to those in 1983, with there being no apparent difference due to the initial organic treatments. The maintenance addition of fertiliser still provided an extra source of available nitrogen. However the levels of extractable nitrate in this year were lower than the ammonium values which was in complete contrast to the previous year's results. The levels of nitrate found in 1983 indicated that there were nitrifying bacteria present within the plots so the very low concentrations found in 1984 must have been caused by some other factor. Leaching was the most probable cause as 1984 had a very wet summer and since nitrate is very readily leached from spoils it will have been lost continually through the season. The slightly higher concentrations found in the maintenance plots indicated that they might have been more capable of recovering from these nitrate losses through leaching.

The levels of total extractable nitrogen from the spoil (Tables 4.9 and 4.10) highlight the fact that the maintenance addition of fertiliser in 1981 still appeared to be enhancing the quantity of available nitrogen in the spoil two and three years later. This could be a direct effect from fertiliser remaining in the spoil, but is more likely to be due to enhanced vegetative growth providing a greater organic pool for mineralisation. The overall trend from the next two years appears to be a reduction in extractable nitrogen from 1983 to 1984. This apparent loss in spoil nitrogen may have been an artifact of sampling after a wet season in 1984 which would have caused the leaching of most of the available nitrate. This loss in spoil nitrogen could be compensated for by the processes of mineralisation and nitrification. However if the total amount of nitrate lost through leaching outweighed the input of nitrogen via rain and fixation by legumes, then there would have been a net nitrogen loss from the system. If this were to happen each year then the reclamation scheme would slowly degenerate and eventually fail. Only the analysis of all the nitrogen containing components in the system can determine to what extent nitrogen has been lost since the onset of the reclamation programme.

4.3.2.2 Phosphorus

Colliery pit heaps usually contain little or no available phosphate, and the more acid the spoil becomes with weathering, the less phosphate is available. This very low availability in colliery spoils is primarily due to the presence of pyrite. When this is oxidised by weathering one of the products is a colloidal amorphous ferric hydroxide which precipitates out as a thin coat over the spoil mineral particles. The resultant large surface area enhances the ability of amorphous ferric hydroxide to adsorb phosphate in large quantities which is more or less irretrievable by non-specific anion exchange (Wingston et al. 1968).

The production of oxide coatings by pyrite weathering causes a correlation between falling pH and increasing phosphate adsorption in the spoil. Liming may improve the situation slightly, but does not reverse the problem because once the oxide film has been formed, liming only stabilises it. This can be observed from Figures 4.5 and 4.6 where phosphate adsorption isotherms were determined on unamended and limed spoil from Baads Colliery, West Lothian. These had pH´s of 2.8 and 6.4 respectively. The limed spoil (Figure 4.2) appears to have reached its adsorption maxima at around 1.25 g P/kg whereas the unlimed material has not attained its maximum by 1.5 g P/kg. In an attempt to get an adsorption maximum figure for the unlimed spoil and also to compare theoretical values of adsorption maxima to observed values, Langmuir isotherms were plotted for the two spoil types (Figures 4.7 and 4.8). The theoretical maximum adsorption, given by the reciprocal of the slope, for the limed spoil was very close to that of the observed value, 1.3 compared to 1.25 g P/kg. The theoretical maximum adsorption for the unlimed spoil lay in the range of about 1.6-1.7 g P/kg depending how the best fit for a straight line was drawn. This fits well with the observed values as the isotherm was approaching a maximum at 1.5 g P/kg.

These adsorption values are extremely high and if there were to be assumed to be 1800 tonnes of spoil per hectare, then these values are equivalent to an adsorption capacity of 2.3 and 3.0 t P/ha for the limed and unlimed spoils respectively. These figures are much higher than would be observed in the field as only the <2 mm fraction was used in the experiment. However they still highlight the great ability the material has for removing phosphate from solution.

Figure 4.5

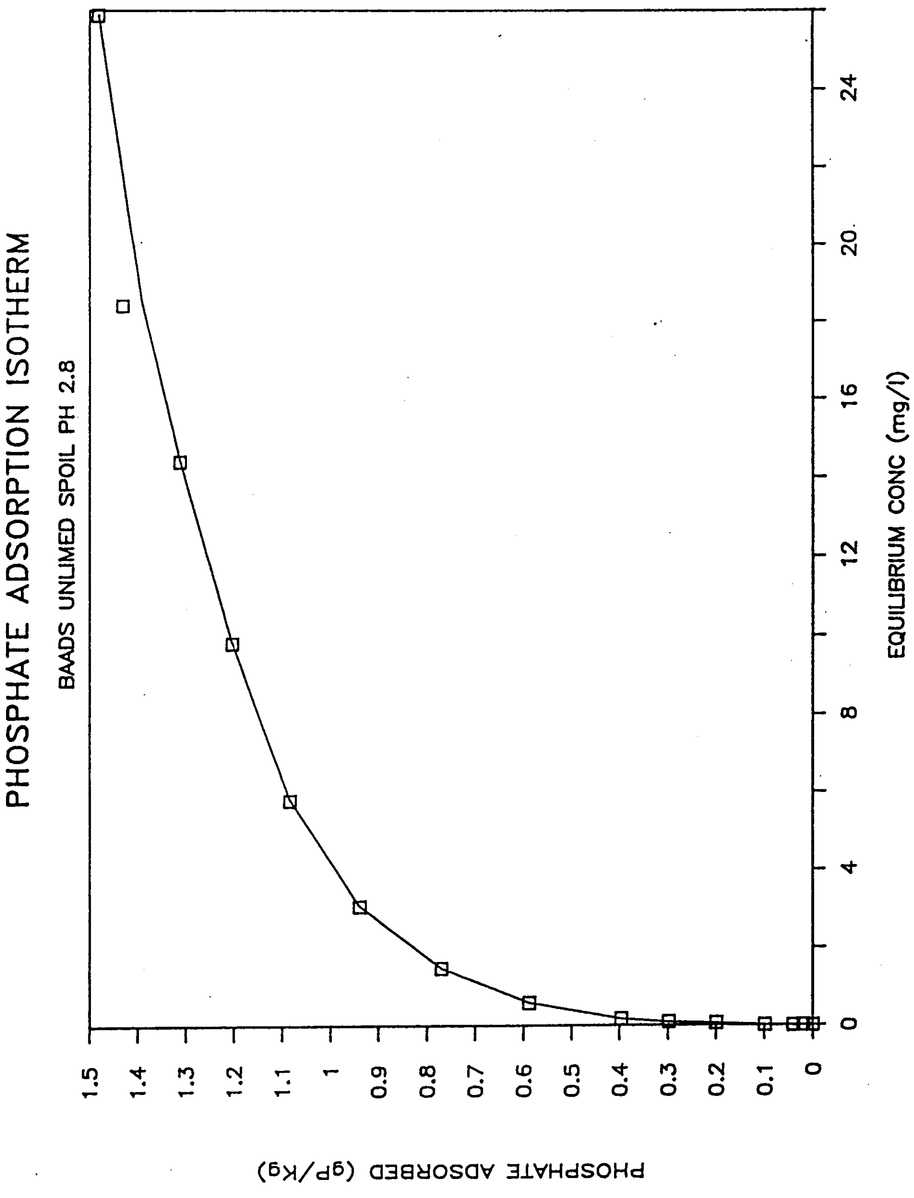

PHOSPHATE ADSORPTION ISOTHERM
BAADS UNLIMED SPOIL PH 2.8
PHOSPHATE ADSORBED (gP/Kg)
1.5
1.4
1.3
1.2
1.1
1
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0
EQUILIBRIUM CONC (mg/l)
0
4
8
12
16
20
24

Figure 4.6

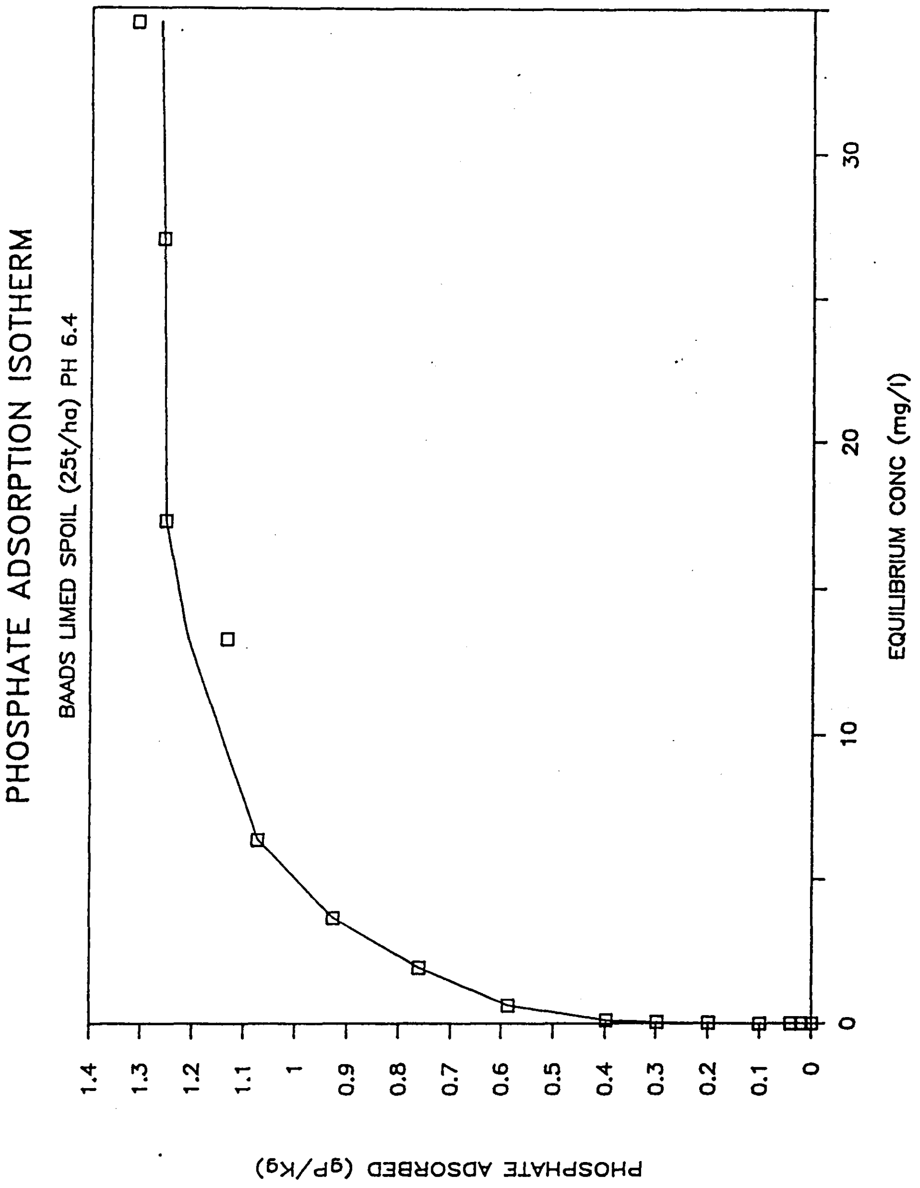

PHOSPHATE ADSORPTION ISOTHERM
BAADS LIMED SPOIL (25t/ha) PH 6.4
PHOSPHATE ADSORBED (gP/Kg)
1.4
1.3
1.2
1.1
1
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0
EQUILIBRIUM CONC (mg/l)
0
10
20
30

Figure 4.7

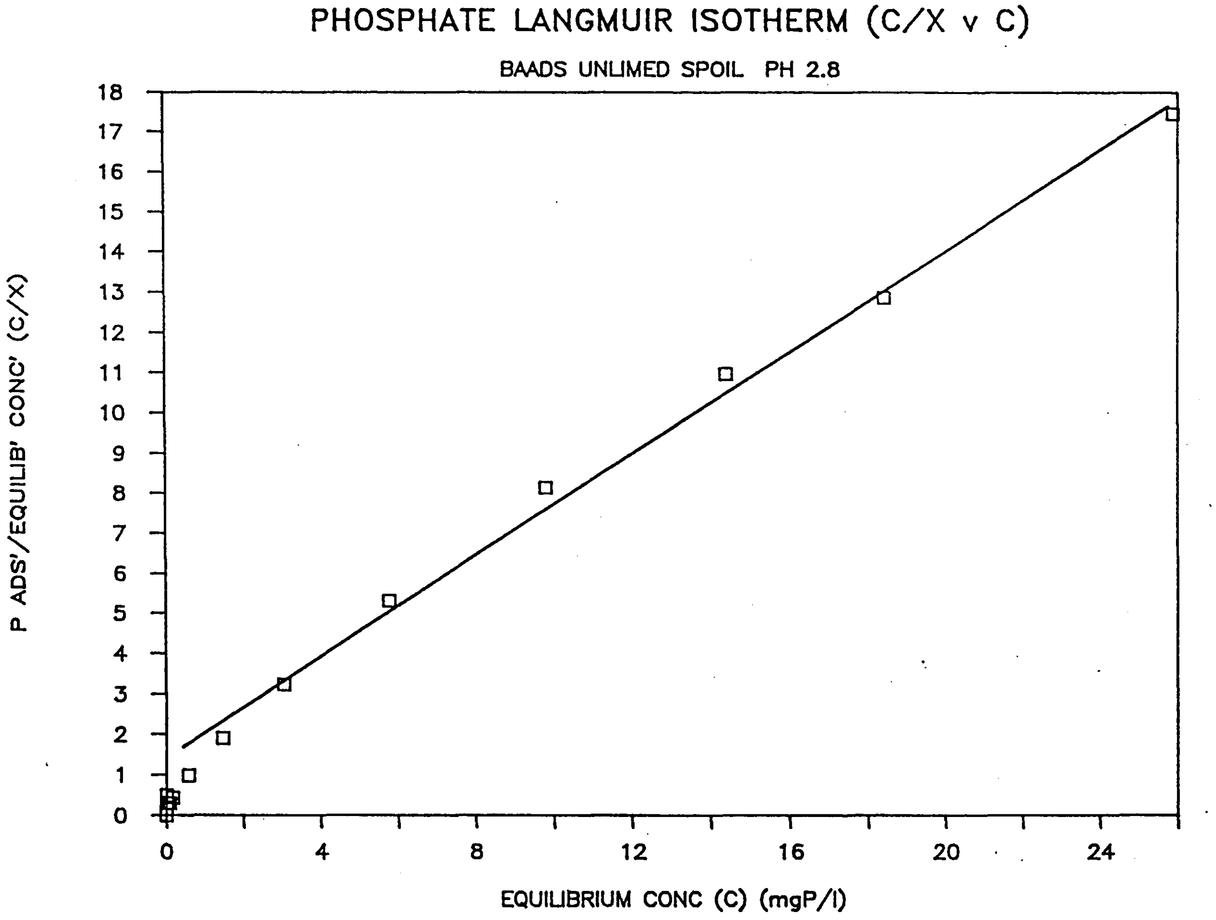
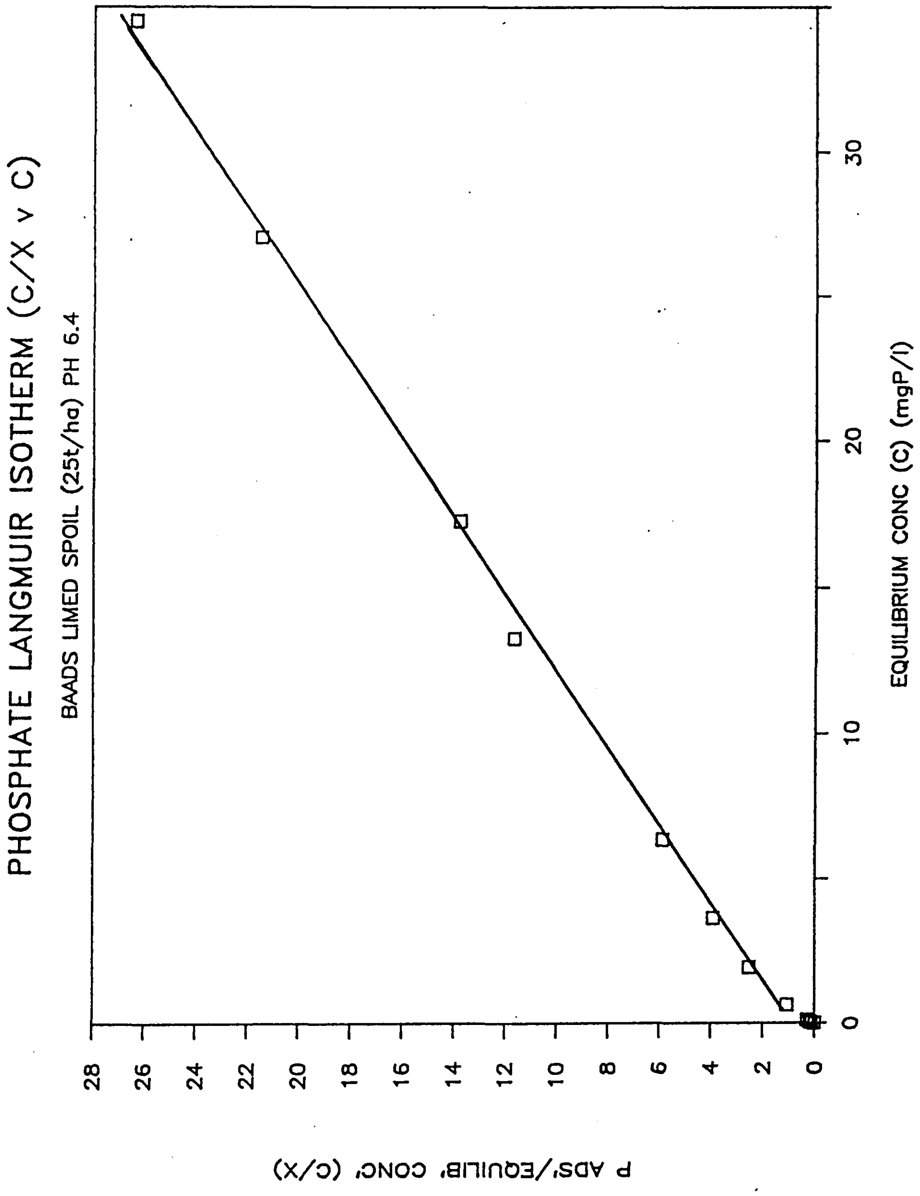

PHOSPHATE LANGMUIR ISOTHERM (C/X v C)
BAADS UNLIMED SPOIL PH 2.8
P ADS'/EQUILIB' CONC' (C/X)
0
1
2
3
4
5
6
7
8
9
10
11
12
13
14
15
16
17
18
EQUILIBRIUM CONC (C) (mgP/l)
0
4
8
12
16
20
24

Figure 4.8


PHOSPHATE LANGMUIR ISOTHERM (C/X v C)
BAADS LIMED SPOIL (25t/ha) PH 6.4
P ADS'/EQUILIB' CONC' (C/X)
28
26
24
22
20
18
16
14
12
10
8
6
4
2
0
EQUILIBRIUM CONC (C) (mgP/l)
0
10
20
30

Acetic acid extractable levels of phosphate were measured in the spoil in 1983 and 1984 (tables 4.11 and 4.12). The extractable values found in the unamended unlimed plots were very low, 0.3-0.4 mg P/kg even after receiving a maintenance addition of fertiliser. These values agree with the general findings of previous studies that extractable phosphate is low in colliery spoil. Palmer (1978) used a number of standard P extractants on spoil from the Yorkshire coalfield and found that the levels of phosphate removed were too close to zero to be of value. Using spoil from a Scottish coalfield, Pulford (1976) could find no acetic acid-extractable phosphate in acid spoil. Fitter et al. (1974) reported a mean of 5.5 mg P/kg for bicarbonate-extractable phosphate in Lancashire spoil.

Liming of the spoil at Baads Colliery appears to have made slightly more phosphate available, (Tables 4.11 and 4.12), but the levels are still very low. The peat and Alginure treatments supplied 4.8 and 0 kg P/ha respectively and show similar levels of extractable phosphate as the unamended plots, indicating that most of this added phosphate has become unavailable. With all three treatments the maintenance fertiliser addition improved the levels of phosphate in the spoil by only a very small amount. The sewage sludge amendment provided about 31 kg P/ha and marginally increased the levels of extractable phosphate over those of the previous three treatments mentioned. The chicken manure used in this study contained a high level of organic phosphate (84 kg

P/ha at application rate used) which was apparently made available for plant uptake with extractable concentrations of phosphate being much higher than for other treatments. The high level of phosphate input may have saturated the majority of specific adsorption sites leaving some phosphate available for non-specific anion exchange. The levels of phosphate in the spoil did not change markedly from 1983 to 1984, apart from the chicken manure treatment. This apparent increase could be due to mineralisation of residual manure, but might also be caused by the large variations between plot and area samples. For the levels of phosphate to be maintained even at these low values, any phosphate removed by the growing vegetation has to be replaced by desorption from the spoil material or from mineralisation of the organic pool within the reclaimed system.

Table 4.11 Acetic acid extractable P (mg/kg) in spoil (1983)

TREATMENT	NO MAINTENANCE	MAINTENANCE
Chicken Manure * + Lime **	21.93 (5.77), 33.58 (39.65), 13.20 (1.73) 22.90 (10.20)	15.33 (0.98), 47.97 (21.80), 40.13 (22.90) 34.48 (17.00)
Sewage Sludge + Lime	1.23 (0.93), 1.69 (1.66), 1.68 (0.27) 1.53 (0.26)	4.36 (2.08), 6.49 (4.06), 3.13 (1.90) 4.66 (1.70)
Alginure + Lime	0.84 (0.26), 1.51 (0.58), 0.65 (0.30) 1.00 (0.45)	1.64 (0.81), 1.19 (0.25), 1.73 (1.64) 1.52 (0.29)
Peat + Lime	0.26 (0.13), 1.93 (0.58), 1.01 (0.81) 1.07 (0.84)	1.16 (0.90), 1.53 (1.00), 1.45 (1.06) 1.38 (0.19)
No amendment + Lime	0.49 (0.24), 1.61 (0.64), 2.00 (0.74) 1.37 (0.78)	0.95 (0.64), 4.46 (2.81), 4.18 (2.09) 3.19 (1.95)
No amendment + No Lime	0.06 (0.00), 0.21 (0.27), 0.57 (0.27) 0.28 (0.26)	0.30 (0.12), 0.24 (0.07), 0.35 (0.29) 0.30 (0.05)

* Mean and standard deviations for triplicate samples from each of areas A, B and C.

** Mean and standard deviation of mean values for the three areas.

Table 4.12 Acetic acid extractable P (mg/kg) in spoil (1984)

TREATMENT	NO MAINTENANCE	MAINTENANCE
Chicken Manure *	63.16 (27.60), 21.10 (10.30), 36.16 (17.70)	20.94 (4.80), 71.81 (27.30), 39.44 (15.50)
+ Lime **	40.14 (21.30)	44.06 (25.75)
Sewage Sludge	3.05 (1.91), 2.75 (0.55), 1.54 (1.57)	6.78 (4.22), 8.62 (3.05), 1.74 (1.55)
+ Lime	2.45 (0.80)	5.71 (3.56)
Alginure	0.81 (0.37), 2.52 (2.38), 0.86 (0.94)	0.54 (0.41), 1.69 (0.74), 1.50 (1.30)
+ Lime	1.40 (0.97)	1.24 (0.61)
Peat	0.61 (0.12), 1.68 (1.13), 0.73 (0.56)	0.79 (0.71), 1.81 (0.44), 1.85 (0.42)
+ Lime	1.01 (0.59)	1.48 (0.60)
No amendment	0.36 (0.12), 2.03 (1.19), 0.63 (0.54)	0.55 (0.16), 1.59 (0.73), 3.52 (3.18)
+ Lime	1.07 (0.86)	1.89 (1.50)
No amendment	0.12 (0.12), 0.41 (0.25), 0.51 (0.19)	0.19 (0.02), 0.39 (0.17), 0.63 (0.48)
+ No Lime	0.35 (0.20)	0.40 (0.22)

* Mean and standard deviations for triplicate samples from each of areas A, B and C.

** Mean and standard deviation of mean values for the three areas.

4.3.2.3 Potassium

Of the three major nutrients, potassium presents the least problem as colliery shale is generally rich in potassium and this may become available by release during weathering. However this availability tends to fall as the colliery spoil becomes acidic, but this tendency can be reversed in unburnt shale by liming. Quantity/intensity relationships for spoil potassium were determined for both unlimed (pH 2.8) and limed (pH 6.4) spoil from Baads Colliery, West Lothian. The intensity factor is expressed as the ratio of potassium activity to the activities of the other dominant cations in solution, usually calcium and magnesium, but for acid spoils aluminium and manganese can be important. The quantity factor is the amount of potassium held on spoil surfaces. The relationship is derived from the Gapon equation for cation exchange:

$$\frac{\text{K exch}}{\text{(Ca + Mg)exch}} \times K = \frac{\text{K soln.}}{[\text{(Ca + Mg)soln}]^{1/2}}$$

This can be rearranged to give:

$$\text{K exch} \times K^{1} = \frac{\text{K soln.}}{[\text{(Ca + Mg)soln}]^{1/2}}$$

where the constant K^{1} incorporates the Gapon constant K and the exchangeable Ca and Mg.

From this, quantity is proportional to intensity and a straight line would be expected. In practice however this does not happen due to the different bonding energies with which potassium is held on soil surfaces. Thus the slope and shape of the quantity/intensity curve can give information about the pools of exchangeable potassium in a spoil and their availability.

There appears to be a marked difference between the unlimed and limed spoils (Figures 4.9 and 4.10). The point at which the lime cuts the x axis is AR_0, the activity ratio of the spoil solution which for unlimed spoil is approaching zero. In the limed spoil AR_0 is 1.3 which is an improvement over the unlimed material, but is still low compared to most soils.

The slope of the line at any point on the curve gives the buffering capacity of the spoil for potassium at that value of AR, ie. the ease with which potassium can be released from the exchange sites as solution potassium is depleted. Thus the steeper the slope, the more able the spoil is to maintain an adequate potassium concentration in solution which is an important factor in terms of potassium availability to plants. The unlimed and limed spoils had values of about 0.13 and 0.21 respectively showing an improvement from the liming treatment, but both are low when compared to normal soils.

Figure 4.9

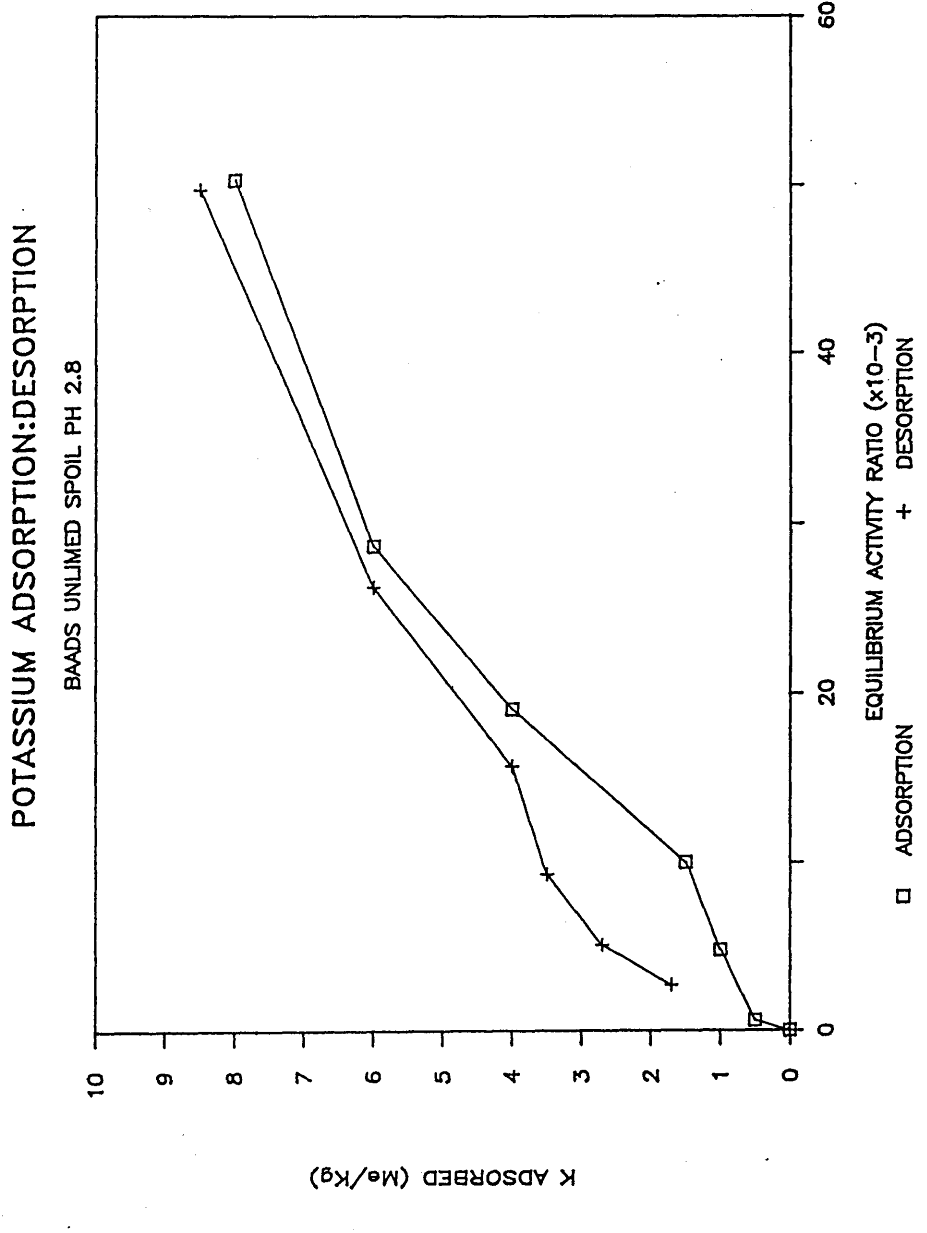
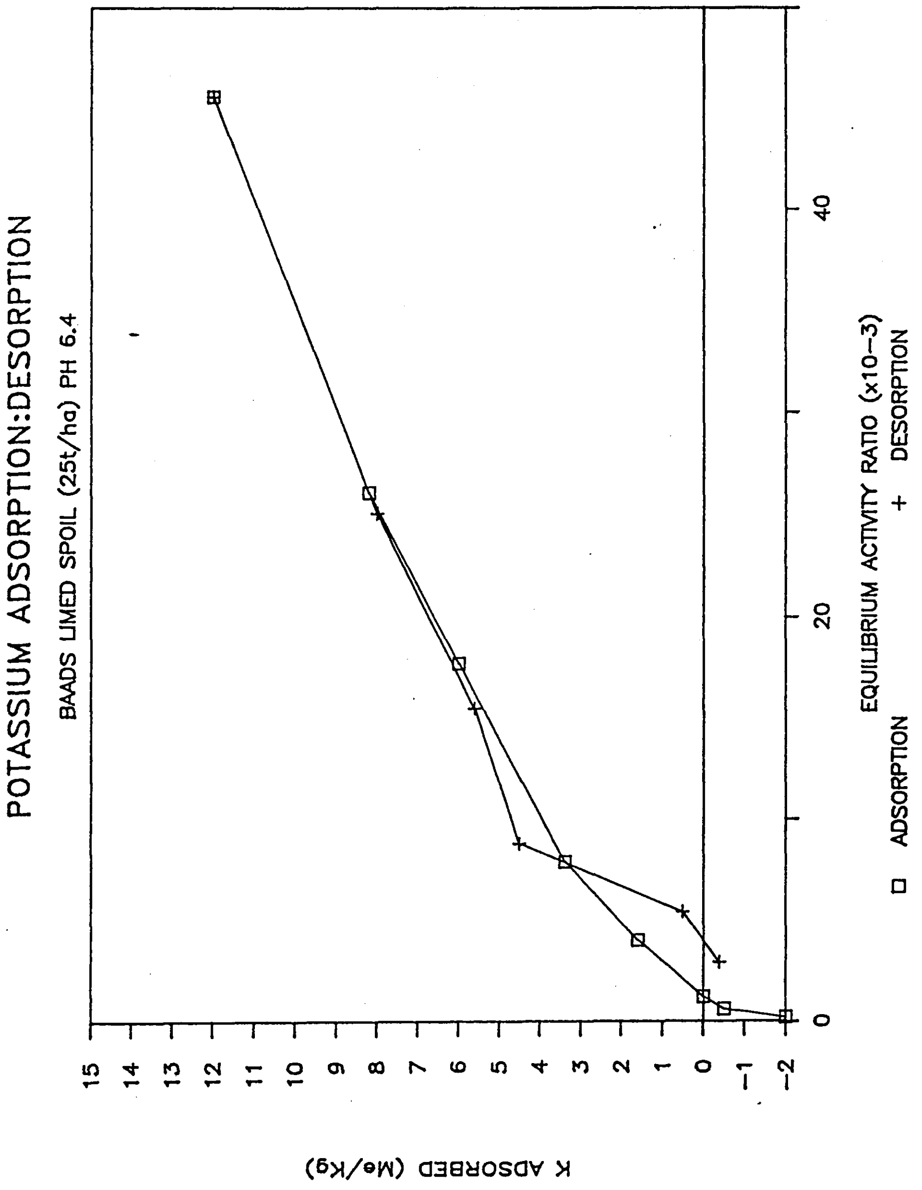

POTASSIUM ADSORPTION:DESORPTION
BAADS UNLIMED SPOIL PH 2.8
K ADSORBED (Me/Kg)
0
1
2
3
4
5
6
7
8
9
10
0
20
40
60
EQUILIBRIUM ACTIVITY RATIO (x10−3)
□ ADSORPTION
+ DESORPTION

Figure 4.10


POTASSIUM ADSORPTION:DESORPTION
BAADS LIMED SPOIL (25t/ha) PH 6.4
K ADSORBED (Me/Kg)
15
14
13
12
11
10
9
8
7
6
5
4
3
2
1
0
−1
−2
0
20
40
EQUILIBRIUM ACTIVITY RATIO (x10−3)
□ ADSORPTION
+ DESORPTION

Measures of exchangeable potassium can be obtained from Q/I curves by extrapolating the linear and curved portions back to the y axis. The linear extrapolation is considered to be potassium held on planar surfaces of clay particles, which are low affinity sites so the potassium is freely exchangeable. The difference between the two is thought to be potassium held mainly in wedge sites at the edges of illites and micaceous mineral lattices. These sites are specific for potassium and so any held there is less freely exchangeable. In the unlimed spoil there appeared to be no exchangeable potassium at all, the majority of it having been removed by leaching under the extremely acidic conditions found in this material (Pulford and Duncan 1978). The limed spoil had a certain amount of exchangeable potassium available, but the majority of this seemed to be held on the wedge sites making it less available to buffer solution concentrations.

From the desorption curves it would appear that all the potassium adsorbed by the limed spoil is freely exchangeable as the desorption curve followed that of adsorption curve. With the unlimed spoil, however, the desorption curve had been displaced above the adsorption line indicating that some of the adsorbed potassium had become fixed and so was not freely exchangeable. Therefore if any potassium was applied to this material a certain proportion would become unavailable for exchange or plant uptake. Consequently liming of acidic spoil not only improves the pH conditions, but increases potassium exchange and availability. This is highlighted by the results for acetic acid-extractable potassium from the experimental plots used in this study (Tables 4.13 and 4.14). The levels in the unlimed plots in both 1983 and 1984 were extremely low, 4.2 and 3.5 mg K/kg respectively. Fertiliser additions improved this to a certain extent, but the values were still less than the plots receiving lime. The levels in the limed plots receiving no maintenance fertiliser were similar for all the amendment, and from one year to the other. The similarity between treatments indicates that by this time it was the spoil and not the amendment that was governing potassium availability. In the plots receiving maintenance the amount of extractable potassium roughly doubled from 1983 to 1984. This could be due to reduced plant uptake as the levels of potassium found in the herbage were lower in 1984 than in 1983 (Table 4.22 and 4.23).

Pulford (1976) found a mean for acetic acid extractable potassium of 152 mg K/kg and Lister (1987) measured a mean of 136 mg K/kg exchangeable potassium, both on spoil from Scotland, so the levels found in this study were fairly low, but probably represent an adequate supply for the growing vegetation.

Table 4.13 Acetic acid extractable K (mg/kg) in spoil (1983)

TREATMENT		NO MAINTENANCE	MAINTENANCE
Chicken Manure	*	70.6 (13.5), 89.7 (20.5), 69.8 (27.1)	85.7 (34.3), 68.2 (9.9), 71.4 (26.5)
+ Lime	**	76.7 (11.3)	75.1 (9.3)
Sewage Sludge		73.0 (16.7), 55.5 (7.3), 53.9 (7.3)	58.7 (14.5), 55.5 (14.5), 55.5 (11.0)
+ Lime		60.8 (10.6)	56.6 (1.8)
Alginure		65.9 (6.0), 72.2 (11.2), 88.9 (7.3)	71.4 (12.6), 63.5 (2.7), 67.4 (11.7)
+ Lime		75.7 (11.9)	67.4 (3.9)
Peat		77.8 (5.5), 88.1 (16.7), 68.2 (11.9)	61.9 (0.0), 72.2 (13.1), 70.6 (13.5)
+ Lime		78.0 (9.9)	68.2 (5.5)
No amendment		65.1 (2.7), 47.6 (9.5), 73.0 (23.5)	67.4 (11.7), 69.8 (12.0), 30.1 (2.7)
+ Lime		61.9 (13)	55.8 (22.3)
No amendment		3.2 (1.4), 6.4 (4.1), 3.2 (1.4)	27.0 (5.5), 9.6 (9.6), 52.4 (5.5)
+ No Lime		4.2 (1.8)	29.7 (21.5)

* Mean and standard deviations for triplicate samples from each of areas A, B and C.

** Mean and standard deviation of mean values for the three areas.

Table 4.14 <u>Acetic acid extractable K (mg/kg) in spoil (1984)</u>

TREATMENT		NO MAINTENANCE	MAINTENANCE
Chicken Manure	*	139.7 (37.2), 86.8 (36.7), 94.5 (12.3)	109.1 (25.6), 172.8 (4.7), 160.1 (16.1)
+ Lime	**	107.0 (28.6)	147.3 (33.7)
Sewage Sludge		79.1 (3.3), 78.4 (12.8), 56.7 (16.7)	193.8 (47.2), 82.9 (1.4), 48.9 (15.7)
+ Lime		71.4 (12.7)	135.2 (55.7)
Alginure		94.0 (23.1), 86.1 (26.6), 69.1 (30.2)	129.7 (22.2), 142.6 (19.9), 152.7 (19.9)
+ Lime		83.1 (12.7)	141.7 (11.5)
Peat		69.0 (6.2), 73.7 (10.2), 77.9 (30.1)	119.1 (21.4), 157.4 (61.9), 98.8 (23.5)
+ Lime		73.5 (4.4)	125.1 (29.7)
No amendment		55.6 (9.0), 63.5 (13.9), 58.3 (28.5)	126.0 (57.6), 88.6 (22.3), 167.9 (64.9)
+ Lime		59.1 (4.0)	127.5 (39.7)
No amendment		3.2 (1.4), 6.4 (4.1), 3.2 (1.4)	27.0 (5.5), 9.6 (9.6), 52.4 (5.5)
+ No Lime		3.5 (1.5)	26.8 (27.1)

* Mean and standard deviations for triplicate samples from each of areas A, B and C.

** Mean and standard deviation of mean values for the three areas.

4.3.3 Herbage

The results of the herbage analysis and also those of the vegetative mat in the following section display only the mean values and variations between the three areas for each treatment. The values for the triplicate samples taken from each area showed a similar degree of variation so they have been omitted to enable a simpler presentation of results.

4.3.3.1. Yield

One of the most important objectives in any reclamation scheme is the production of a dense, healthy vegetative cover that improves the visual appearance and stabilises the spoil. If the reclaimed land was not intended for agricultural purposes then the likelihood of any maintenance aftercare is minimal. If this is the case then it is essential to have a self-sustaining system that can generate good yields from year to year. The results presented in Table 4.15 show the effect of the various organic amendments in stimulating vegetative growth. The addition of manure-type amendments (chicken manure and sewage sludge) resulted in much higher yields initially, but this difference steadily declined. The peat and Alginure treatments gave poor yields initially but thereafter behaved silmilarly to the unamended plots. A fact of greater importance is that the actual yields decreased from one year to the next, indicating that the system is slowly degenerating. The yields for the growing season in 1983 and 1984 are presented in Tables 4.16 and 4.17 respectively. In the original plots that received the Alginure, peat and no amendment treatments the yield had apparently levelled off in the range of 0.5-1 t/ha. However the chicken manure and sewage sludge treatments, which had high initial yields, were still dropping but remained greater than the other treatments. These yields were similar to those found by Marrs et al. (1980) for naturally grazed reclaimed china clay wastes and Fyles et al. (1985) for reclaimed coal mine waste.

Table 4.15 Vegetation yield on plots receiving no maintenance: expressed as percentage of control (no organic amendment)

Treatment/Year	1980*	1982*	1983	1984
Chicken Manure	722	499	310	226
Sewage Sludge	226	288	250	227
Alginure	34	88	106	157
Peat	62	105	83	112

* Devlin unpublished

Table 4.16 Herbage yield 1983 t/ha dry matter

	No maintenance	Maintenance
Chicken Manure + Lime	1.9 (0.88)	2.8 (0.63)
Sewage Sludge + Lime	1.5 (0.30)	2.6 (0.32)
Alginure + Lime	0.64 (0.09)	1.9 (0.41)
Peat + Lime	0.51 (0.21)	1.6 (0.39)
No Amendment + Lime	0.61 (0.23)	1.2 (0.11)

Table 4.17 Herbage yield 1984 t/ha dry matter

	No maintenance	Maintenance
Chicken Manure + Lime	1.3 (0.24)	2.0 (0.49)
Sewage Sludge + Lime	1.3 (0.68)	2.0 (0.33)
Alginure + Lime	0.90 (0.32)	1.1 (0.23)
Peat + Lime	0.65 (0.07)	1.4 (0.15)
No Amendment + Lime	0.58 (0.26)	0.79 (0.34)

Data presented are the mean values and standard deviation over the three areas.

The half-plots that received fertiliser in 1981 showed improved yields compared to the corresponding unmaintained ones two and three years after fertiliser addition. This improvement was gradually reducing indicating the removal of available nutrients. Bloomfield et al. (1982) demonstrated the effect of fertilisation on vegetation yield on reclaimed colliery spoil and deduced that nitrogen deficiency was the major limiting factor. They also showed that this effect was reduced in the second year after fertilisation.

The indications are that insufficient amounts of the major nutrients were being released by mineralisation to maintain yields, either because of too small a nutrient capital or the failure of the mineralisation process. Evidence from other studies (Marrs et al. 1982; Skeffington and Bradshaw 1982) indicate that it is the lack of the nutrient capital that is the major problem.

4.3.3.2 Nutrient content of herbage

i) Nitrogen

The nitrogen content of the herbage expressed as a percentage of the dry matter (Tables 4.18 and 4.19) indicated that there was no difference due to the various treatments used. Neither was there any increase in the plots that received maintenence fertiliser additions. The values which lie in the range of 0.67-0.9% for 1983 and 1.1-1.4% for 1984 were quite low even for vegetation grown on reclaimed waste material and indicate that nitrogen is deficient within the system. Although the increased yields (Tables 4.16 and 4.17) in the chicken manure, sewage sludge and maintenance plots suggest that there was more nitrogen available, the levels were still too low to improve the nitrogen composition of the vegetation. The higher concentrations found in 1984 could be due to a combination of lower yields which would reduce the competition for available nitrogen, and the fact that the spoil was too moist which might have increased the rate of nitrogen mineralisation which is moisture dependent.

Table 4.18 Nitrogen content of herbage (%N) in dry matter (1983)

	No maintenance	Maintenance
Chicken Manure + Lime	0.82 (0.21)	0.84 (0.17)
Sewage Sludge + Lime	0.76 (0.32)	0.78 (0.14)
Alginure + Lime	0.83 (0.18)	0.70 (0.22)
Peat + Lime	0.90 (0.25)	0.72 (0.28)
No Amendment + Lime	0.90 (0.26)	0.67 (0.20)

Data presented are the mean values and standard deviation over the 3 areas.

Table 4.19 Nitrogen content of herbage (%N) in dry matter (1984)

	No maintenance	Maintenance
Chicken Manure + Lime	1.1 (0.12)	1.1 (0.13)
Sewage Sludge + Lime	1.1 (0.27)	1.1 (0.08)
Alginure + Lime	1.3 (0.26)	1.3 (0.22)
Peat + Lime	1.3 (0.16)	1.2 (0.25)
No Amendment + Lime	1.4 (0.19)	1.3 (0.25)

Data presented are the mean values and standard deviation over the 3 areas.

ii) Phosphorus

The phosphorus content of the herbage was very similar for all the treatments used in this study over both years (Tables 4.20 and 4.21). Even the increased levels of spoil phosphate in the maintenance plots, and the high levels found in the plots that received chicken manure had no effect on the amount of phosphorus found in the vegetation. This would indicate that there was some other factor limiting phosphate uptake. The most obvious is the very low availability of nitrogen within the spoil. However the phosphate levels were so low in all but the chicken manure plots, that if nitrogen was supplied in sufficient quantities, then phosphate would probably be the next limiting factor to healthy growth.

Table 4.20 Phosphorus content of herbage (%P) in dry matter (1983)

	No maintenance	Maintenance
Chicken Manure + Lime	0.20 (0.02)	0.20 (0.02)
Sewage Sludge + Lime	0.17 (0.03)	0.19 (0.01)
Alginure + Lime	0.14 (0.01)	0.15 (0.03)
Peat + Lime	0.14 (0.02)	0.15 (0.03)
No Amendment + Lime	0.15 (0.04)	0.15 (0.02)

Table 4.21 Phosphorus content of herbage (%P) in dry matter (1984)

	No maintenance	Maintenance
Chicken Manure + Lime	0.22 (0.04)	0.22 (0.03)
Sewage Sludge + Lime	0.21 (0.03)	0.20 (0.01)
Alginure + Lime	0.17 (0.02)	0.20 (0.06)
Peat + Lime	0.20 (0.04)	0.17 (0.02)
No Amendment + Lime	0.18 (0.01)	0.15 (0.02)

Data presented are the mean values and standard deviation over the 3 areas.

iii) Potassium

The levels of potassium found in the vegetation were again low (Tables 4.22 and 4.23) when compared to herbage grown on natural soils which tends to have potassium contents of 2-3% of the dry matter. The similarity between treatments reflected the fact that potassium availability was governed by weathering of the spoil material rather than additions by fertiliser or amendments and since the levels of available potassium in the spoil should not be limiting, there must be another factor governing the small amounts found in the vegetation. It has been proposed that potassium is removed from leaves largely by leaching rather than retranslocation (Epstein 1972) and so the wet growing season and autumn in 1984 may have enhanced this process, resulting in the lower percentages of potassium found in that year´s vegetation compared to those of the previous year.

Table 4.22 Potassium content of herbage (%K) in dry matter (1983)

	No maintenance	Maintenance
Chicken Manure + Lime	1.3 (0.19)	1.4 (0.15)
Sewage Sludge + Lime	1.3 (0.22)	1.3 (0.11)
Alginure + Lime	1.2 (0.14)	1.1 (0.08)
Peat + Lime	1.0 (0.10)	1.2 (0.17)
No Amendment + Lime	1.1 (0.25)	1.1 (0.20)

Table 4.23 Potassium content of herbage (%K) in dry matter (1984)

	No maintenance	Maintenance
Chicken manure + Lime	0.66 (0.10)	0.55 (0.01)
Sewage Sludge + Lime	0.75 (0.18)	0.55 (0.09)
Alginure + Lime	0.77 (0.15)	0.74 (0.14)
Peat + Lime	0.86 (0.08)	0.62 (0.04)
No Amendment + Lime	0.86 (0.11)	0.56 (0.11)

Data presented are the mean values and standard deviation over the 3 areas.

4.3.4 Litter Accumulation

One of the major factors governing the ability of a reclamation scheme to maintain herbage growth is nutrient cycling which occurs through retranslocation within plants and through litter decomposition processes. However accumulation of standing dead material may block this nutrient recycling (Marrs, Granlund and Bradshaw 1980). It has been observed in Montana that the growth of vegetation on coal mine spoils had reached levels comparable with adjacent undisturbed rangeland within two years, but litter and standing dead material may be expected to reach four to seven times natural levels in five years (Sindelar 1979). Schafer and Nielson (1979) have suggested that high litter accumulations can block nutrient cycling and increase C:N ratios in reclaimed spoil leading to decreased plant available nitrogen.

4.3.4.1 Yield

During spoil and vegetation sampling it became apparent that this process of litter accumulation was taking place on the experimental plots at Baads Colliery, West Lothian. This material was therefore collected for yield measurements and analysis to determine to what extent the three major nutrients nitrogen, phosphorus and potassium were being tied up in this fraction. Tables 4.24 and 4.25 show the litter yields for the years 1983 and 1984 respectively.

Table 4.24 <u>Vegetation mat yield 1983 t/ha dry matter</u>

		No maintenance		Maintenance	
Chicken Manure + Lime	<2mm	1.3	(0.31)	1.3	(0.26)
	>2mm	2.7	(0.45)	3.2	(0.41)
	Total	4.0		4.5	
Sewage Sludge + Lime	<2mm	0.6	(0.13)	0.8	(0.16)
	>2mm	1.8	(0.28)	2.2	(0.30)
	Total	2.4		3.0	
Alginure + Lime	<2mm	0.6	(0.10)	0.7	(0.12)
	>2mm	1.9	(0.27)	2.1	(0.23)
	Total	2.5		2.8	
Peat + Lime	<2mm	0.7	(0.09)	0.8	(0.15)
	>2mm	2.0	(0.28)	2.9	(0.61)
	Total	2.7		3.7	
No Amendment + Lime	<2mm	0.5	(0.24)	0.5	(0.20)
	>2mm	1.8	(0.16)	2.3	(0.23)
	Total	2.3		2.8	

Data presented are the mean values and standard deviation over the three areas.

Table 4.25 Vegetation mat yield 1984 t/ha dry matter

		No maintenance		Maintenance	
Chicken Manure + Lime	<2mm	2.7	(0.60)	3.4	(1.3)
	>2mm	3.5	(0.90)	4.2	(1.0)
	Total	6.2		7.6	
Sewage Sludge + Lime	<2mm	2.0	(0.50)	2.1	(0.55)
	>2mm	3.6	(0.08)	3.5	(1.09)
	Total	5.6		5.6	
Alginure + Lime	<2mm	1.9	(0.80)	1.6	(0.16)
	>2mm	2.0	(1.07)	2.7	(0.85)
	Total	3.9		4.3	
Peat + Lime	<2mm	1.6	(0.48)	2.3	(0.88)
	>2mm	1.7	(0.11)	2.7	(1.51)
	Total	3.3		5.0	
No Amendment + Lime	<2mm	1.5	(0.53)	1.3	(0.70)
	>2mm	1.7	(0.93)	2.1	(0.20)
	Total	3.2		3.4	

Data presented are the mean values and standard deviation over the three areas.

The differences between treatments tend to reflect the differences in vegetation yields that have been observed during the course of this reclamation scheme. The manures yielded high levels of vegetation initially which has led to a greater accumulation of dead material. The maintenance fertiliser which stimulated vegetative growth has also resulted in increased litter levels. As the nutrient status of the vegetation declines, so will its decomposition rate and this is exhibited by the increase in litter between 1983 and 1984 which approximates to the herbage yield in 1983. This is similar to the findings of King (1979) who suggested that the observed accumulation of detritus on a six year old revegetated site was primarily the result of one season's deposition rather than a long-term trend.

The proportion of the total accumulated litter material attributable to the less than two millimetre fraction was greater in 1984 than in 1983. The continuously wet condition of the material through the season probably led to increased chemical and biological breakdown of the larger unhumified material. After five years development in the experimental plots used in this study, the accumulation of litter gives yields two to three times that of the growing vegetation on a dry matter basis which is similar to the findings of Fyles et al. (1985) and Marrs et al. (1980).

The extremely harsh physical and chemical nature of coal spoil material has led to there being extremely low if not non-existant populations of earthworms and other mesofauna, which are responsible for the majority of litter breakdown and incorporation in natural soil systems. Thus this litter layer has accumulated and as will be seen ties up a large proportion of the major nutrients that would otherwise be available for plant uptake.

4.3.4.2 Nutrient composition of litter

The general trend for herbaceous plants is to retranslocate nutrients back down into the rooting system at the onset of senescence. This happens to an even greater extent in plants grown under nutrient stress leading to very nutrient poor litter that is resistant to decomposition. Analysis of the litter collected in the years 1983 and 1984 was carried out and the results are presented below.

i) Nitrogen

Contrary to what was expected the levels of nitrogen found in the litter (Table 4.26 and 4.27) were slightly higher than those of the vegetation. The plots receiving maintenance fertiliser had higher levels than their counterparts in 1983, but this trend was not observed in 1984. As has been seen for the vegetation, the amendment treatments had no effect on the content of the litter, they appeared to affect only the yield.

Table 4.26 Nitrogen content of mat (%N in dry matter) (1983)

	No Maintenance		Maintenance	
	<2mm	>2mm	<2mm	>2mm
Chicken Manure + Lime	1.3 (0.24)	0.86 (0.13)	2.0 (0.13)	1.5 (0.22)
Sewage Sludge + Lime	1.1 (0.13)	0.83 (0.18)	1.9 (0.08)	1.3 (0.17)
Alginure + Lime	1.1 (0.08)	0.74 (0.09)	1.8 (0.20)	1.2 (0.14)
Peat + Lime	1.0 (0.11)	0.62 (0.10)	1.8 (0.15)	1.4 (0.19)
No Amendment + Lime	1.2 (0.14)	0.74 (0.21)	1.7 (0.21)	1.3 (0.25)

Table 4.27 Nitrogen content of mat (%N in dry matter) (1984)

	No Maintenance		Maintenance	
	<2mm	>2mm	<2mm	>2mm
Chicken Manure + Lime	2.0 (0.29)	1.3 (0.10)	1.9 (0.10)	1.6 (0.23)
Sewage Sludge + Lime	1.9 (0.04)	1.5 (0.47)	2.0 (0.07)	1.5 (0.14)
Alginure + Lime	1.8 (0.20)	1.5 (0.36)	1.8 (0.46)	1.6 (0.28)
Peat + Lime	1.7 (0.18)	1.5 (0.18)	1.7 (0.07)	1.8 (0.26)
No Amendment + Lime	2.0 (0.13)	1.7 (0.16)	1.7 (0.30)	1.6 (0.30)

At the onset of reclamation there would have been no nutrient shortage enabling the first few years' vegetation to have nutrient concentrations similar to those found in natural systems. This would lead to the accumulation of plant litter with reasonable levels of the major nutrients, the remains of which may explain the higher concentrations of nitrogen found in the litter five years after reclamation when the levels in the vegetation were low. Another possibility could be that on sampling some very fine shale material may have been incorporated which would increase the apparent nitrogen concentration.

ii) Phosphorus

The concentrations of phosphorus in the litter (Tables 4.28 and 4.29) were very low, but similar to those of the vegetation. The values were uniform despite the amendment or fertiliser regime and are constant from one year to the next.

Table 4.28 Phosphorus content of mat (%P in dry mat) (1983)

	No Maintenance		Maintenance	
	<2mm	>2mm	<2mm	>2mm
Chicken Manure + Lime	0.25 (0.03)	0.19 (0.04)	0.20 (0.05)	0.18 (0.03)
Sewage Sludge + Lime	0.15 (0.02)	0.16 (0.03)	0.17 (0.04)	0.16 (0.05)
Alginure + Lime	0.13 (0.02)	0.13 (0.01)	0.14 (0.01)	0.14 (0.01)
Peat + Lime	0.12 (0.01)	0.11 (0.03)	0.13 (0.02)	0.14 (0.02)
No Amendment + Lime	0.14 (0.03)	0.12 (0.02)	0.14 (0.01)	0.15 (0.02)

Table 4.29 Phosphorus content of mat (%P in dry matter) (1984)

	No Maintenance		Maintenance	
	<2mm	>2mm	<2mm	>2mm
Chicken Manure + Lime	0.22 (0.02)	0.19 (0.05)	0.22 (0.02)	0.22 (0.02)
Sewage Sludge + Lime	0.17 (0.02)	0.18 (0.03)	0.25 (0.05)	0.23 (0.04)
Alginure + Lime	0.15 (0.02)	0.15 (0.02)	0.16 (0.03)	0.19 (0.03)
Peat + Lime	0.14 (0.02)	0.16 (0.03)	0.15 (0.02)	0.21 (0.02)
No Amendment + Lime	0.17 (0.03)	0.18 (0.03)	0.16 (0.03)	0.18 (0.01)

iii) Potassium

Potassium, as has been stated earlier, can be lost via leaching from the leaves, so the concentrations found in litter would be expected to be lower than in the vegetation. The results (Tables 4.30 and 4.31) support this theory with the more humified material (<2 mm) having lower concentrations than the less decomposed (>2 mm) material as it is more susceptible to leaching and had a greater surface area. The potassium levels, as with nitrogen and phosphorus, were not effected either amendment or fertiliser treatment.

The use of nutrient concentrations can be misleading when the objective is to differentiate between the effectiveness of various treatments in the reclamation of coal mine waste, especially when the nutrient availability is limiting growth. However when the concentration and yields are combined to give the overall nutrient content of the vegetation and litter in kg ha^{-1} then the difference between treatments becomes more apparent.

Table 4.30 Potassium content of mat (%K in dry matter) (1983)

	No Maintenance		Maintenance	
	<2mm	>2mm	<2mm	>2mm
Chicken Manure + Lime	0.41 (0.10)	1.13 (0.25)	0.25 (0.06)	0.66 (0.24)
Sewage Sludge + Lime	0.43 (0.07)	1.05 (0.21)	0.26 (0.08)	0.84 (0.31)
Alginure + Lime	0.52 (0.16)	1.1 (0.11)	0.25 (0.02)	0.67 (0.14)
Peat + Lime	0.52 (0.16)	1.1 (0.11)	0.25 (0.02)	0.67 (0.14)
No Amendment + Lime	0.52 (0.16)	1.17 (0.31)	0.28 (0.05)	0.83 (0.09)

Table 4.31 Potassium content of mat (%K in dry matter) (1984)

	No Maintenance		Maintenance	
	<2mm	>2mm	<2mm	>2mm
Chicken Manure + Lime	0.31 (0.06)	0.48 (0.14)	0.33 (0.04)	0.41 (0.22)
Sewage Sludge + Lime	0.23 (0.08)	0.50 (0.27)	0.26 (0.05)	0.44 (0.06)
Alginure + Lime	0.29 (0.17)	0.58 (0.16)	0.29 (0.09)	0.59 (0.09)
Peat + Lime	0.45 (0.20)	0.53 (0.17)	0.25 (0.04)	0.63 (0.27)
No Amendment + Lime	0.38 (0.14)	0.65 (0.18)	0.26 (0.04)	0.49 (0.03)

4.3.5 Nutrient budgets

An important factor in any reclamation scheme is maintaining a sufficient nutrient capital to sustain successive years of good vegetative cover. However coalmine waste is very susceptible to nutrient leaching, especially nitrogen, prior to the establishment of the vegetation.

The total levels of nitrogen, phosphorus and potassium were determined in the spoil, vegetation and dead plant litter in 1983 and 1984 to determine the nutrient status of the developing ecosystem due to the various amendments used in this study. Using the values from fertiliser and amendments inputs (Tables 4.1-4.4) it was possible to determine whether there had been a net loss or accumulation of the three major nutrients, four and five years after reclamation.

The values were expressed on a kg ha^{-1} basis with the vegetation and litter results being calculated by combining the nutrient concentration (%) with the yield, and the spoil by assuming a bulk density of 1.2 t m^{-3} and a rooting depth of 15 cm. This would yield 1,800 t of spoil per hectare.

4.3.5.1 Nitrogen

In the no maintenance plots sampled in 1983 (Table 4.32) the chicken manure treatment had the highest total level of nitrogen remaining, 65 kg ha^{-1} with the other treatments having values in the range 35-44 kg ha^{-1}. The two organic manures, chicken manure and sewage sludge, which supplied high initial levels of nitrogen had only 34 and 29 percent respectively of the original input left in the system. However in the plots that received no excess nitrogen above the fertiliser dosage, there was eighty to ninety percent of the original amount remaining. This would appear to confirm the fact that high levels of nitrogen were lost via leaching immediately after application and that this loss increased with higher initial inputs. The maintenance addition of fertiliser increased the total level of nitrogen by 20-45 kg ha^{-1}, with the greater increases being found in the plots with higher vegetation yields which appeared to be more able to utilise this added nitrogen before it was lost.

The levels of nitrogen found in 1984 (Table 4.33) had increased showing an accumulation of 25 to 50 kg N ha^{-1} and in one case 70 kg ha^{-1} (sewage sludge - no maintenance). This accumulation of nitrgogen was of a similar level to that found by Palmer and Chadwick (1985) for colliery spoil fertilised by ammonium sulphate.

The majority of the nitrogen that had accumulated in the experimental plots was found in the dead litter material. Fifty to sixty percent of the total nitrogen in 1983 increasing to seventy to eighty percent in 1984 was found in this material. The low decomposition of this litter resulted in a mat of dead vegetation building up on the surface of the coal spoil, the depth of which varied with original treatment. This accumulation of detritus removed a large proportion of the total nitrogen from the nitrogen cycle which is detrimental to the development of a self-sustaining ecosystem.

Table 4.32 Total nitrogen in the system (kg ha^{-1}) 1983

		No Maintenance	Maintenance
Chicken Manure + Lime	Spoil	9.81	13.84
	Litter	40.51	72.72
	Vegetation	15.33	23.60
	Total	65.65	110.16
Sewage Sludge + Lime	Spoil	10.47	17.06
	Litter	21.84	44.64
	Vegetation	11.47	20.04
	Total	43.78	81.74
Alginure + Lime	Spoil	10.69	14.58
	Litter	20.90	38.22
	Vegegation	5.31	13.02
	Total	36.90	65.82
Peat + Lime	Spoil	11.61	15.98
	Litter	19.26	54.26
	Vegetation	4.59	11.52
	Total	35.46	81.76
No Amendment + Lime	Spoil	15.12	17.53
	Litter	19.42	37.28
	Vegetation	5.49	8.17
	Total	40.03	62.98
No Amendment + No Lime	Spoil	19.47	31.82
	Litter	-	-
	Vegetation	-	-
	Total	19.47	31.82

Table 4.33 Total nitrogen in the system (kg ha^{-1}) 1984

		No Maintenance	Maintenance
Chicken Manure + Lime	Spoil	3.92	11.88
	Litter	98.33	129.14
	Vegetation	14.02	21.80
	Total	116.27	162.82
Sewage Sludge + Lime	Spoil	5.18	16.25
	Litter	91.87	93.71
	Vegetation	15.18	21.80
	Total	112.23	131.76
Alginure + Lime	Spoil	6.41	13.50
	Litter	63.24	74.07
	Vegetation	11.43	14.11
	Total	81.08	101.68
Peat + Lime	Spoil	7.54	6.08
	Litter	53.46	86.86
	Vegetation	8.77	16.35
	Total	69.77	109.29
No Amendment + Lime	Spoil	6.59	13.93
	Litter	50.14	54.46
	Vegetation	8.35	9.95
	Total	65.08	78.34
No Amendment + No Lime	Spoil	28.45	18.82
	Litter	-	-
	Vegetation	-	-
	Total	28.45	18.82

Even if this litter nitrogen were to become available, the levels accumulated were small compared to organic nitrogen in soils. Most soils contain at least 2,000 kg N ha^{-1} to a depth of 15 cm (Stevenson 1982a), and 700 kg N ha^{-1} has been considered to be the minimum level of nitrogen accumulation at which an ecosystem would become self-sustaining (Dancer, Handley and Bradshaw 1977a). However Bradshaw (1983) has estimated that a nitrogen capital of about 1,600 kg N ha^{-1} is required to sustain a vegetative cover based on a requirement of 100 kg N ha^{-1} yr^{-1} and an organic matter decomposition rate typical of temperate soils.

At the experimental sites at Baads, assuming an accumulation rate of 50 kg N ha^{-1} yr^{-1} and good incorporation and decomposition of the litter material, it would still take 10-12 years to reach a nitrogen capital of 700 kg ha^{-1}.

4.3.5.2 Phosphorus

Of the four organic amendments used in this trial, only chicken manure supplied sufficient phosphorus to maintain reasonable levels within the spoil (Table 4.34). The high phosphate adsorbing ability of the spoil material removed most of the phosphorus added from the other treatments leaving only 2-3 kg P ha^{-1} in the spoil in 1983. The small quantity of phosphorus in the sewage sludge (30 kg ha^{-1}) treatment enabled a response in spoil levels to be observed due to the maintenance fertiliser additions, but this was not detected in the Alginure, peat and no-amendment plots. The spoil levels of phosphate in

1984 were similar to those of the previous year for the Alginure, peat and no amendment treatments. However the levels in the chicken manure and sewage sludge plots increased slightly, possibly through mineralisation or desorption from the soil.

The increase in the total levels of phosphorus in the system between 1983 and 1984 can be attributed mainly to the increased levels found in the litter layer which accounted for about fifty percent of the total in 1983 increasing to around sixty percent in 1984 for all save the chicken manure treatment. The spoil appeared to be capable of maintaining these low levels of available phosphorus even though successive years of vegetative uptake were being tied up in this dead litter pool.

In the chicken manure plots the quantity of phosphorus remaining was fifty five and seventy percent for the unmaintained and maintained plots respectively in 1983 and this increased to ninety percent in 1984. Of this only a very small amount was found in the litter, roughly fifteen percent, and an even smaller quantity in the vegetation. The amount of phosphorus remaining in the system under the various treatments used reflected to a large extent the quantities that were added originally with chicken manure >> sewage sludge > Alginure, peat and no amendment.

There was evidence of improved levels due to the maintenance addition of fertiliser phosphorus, but this was mainly due to the increased yields of vegetation and litter, with no apparent improvement in spoil levels.

Table 4.34 Total phosphorus in the system (kg ha^{-1}) 1983

		No Maintenance	Maintenance
Chicken Manure + Lime	Spoil	41.22	62.06
	Litter	8.38	8.36
	Vegetation	3.74	5.62
	Total	53.34	76.04
Sewage Sludge + Lime	Spoil	2.75	8.39
	Litter	3.78	4.88
	Vegetation	2.57	4.88
	Total	9.10	18.15
Alginure + Lime	Spoil	1.80	2.74
	Litter	3.25	3.92
	Vegetation	0.89	2.79
	Total	5.94	9.45
Peat + Lime	Spoil	1.93	2.48
	Litter	3.04	5.10
	Vegetation	0.71	2.40
	Total	5.68	9.98
No Amendment + Lime	Spoil	2.46	5.74
	Litter	2.86	4.15
	Vegetation	0.91	1.83
	Total	6.23	11.72
No Amendment + No Lime	Spoil	0.50	0.54
	Litter	-	-
	Vegetation	-	-
	Total	0.50	0.54

Table 4.35 Total phosphorus in the system (kg ha^{-1}) 1984

		No Maintenance	Maintenance
Chicken Manure + Lime	Spoil	72.25	79.30
	Litter	12.66	16.67
	Vegetation	2.88	4.40
	Total	87.79	100.37
Sewage Sludge + Lime	Spoil	4.41	10.28
	Litter	9.81	13.11
	Vegetation	2.77	4.00
	Total	16.99	27.39
Alginure + Lime	Spoil	2.52	2.23
	Litter	5.80	7.79
	Vegetation	1.53	2.24
	Total	9.85	12.26
Peat + Lime	Spoil	1.82	2.66
	Litter	4.95	9.14
	Vegetation	1.30	2.40
	Total	8.07	14.20
No Amendment + Lime	Spoil	1.93	3.40
	Litter	5.66	5.74
	Vegetation	1.04	1.18
	Total	8.63	10.32
No Amendment + No Lime	Spoil	0.63	0.72
	Litter	-	-
	Vegetation	-	-
	Total	0.63	0.72

4.3.5.3 Potassium

As would be expected for potassium, the total levels found within the system showed no relation to the original levels applied and were dominated completely by weathering of the background material. For all the treatments used there was net accumulation of potassium, the majority of which was to be found in the spoil (Tables 4.36 and 4.37). However the chicken manure treatment did supply four to five times the amount of potassium than the sewage sludge and the peat which resulted in the quantities being higher than for the other treatments. In 1983 any increase due to the maintenance treatment was not apparent. However in 1984 these plots had roughly twice the amount of available potassium in the spoil than the previous year. The quantity of potassium stored in the litter and vegetation was much lower (40-60%) in 1984 than it was in 1983. As has been mentioned earlier, the much wetter conditions in 1984 probably led to enhanced leaching from the vegetative material.

Table 4.36 Total potassium in the system (kg ha^{-1}) 1983

		No Maintenance	Maintenance
Chicken Manure + Lime	Spoil	138	135
	Litter	35.8	24.4
	Vegetation	25.0	39.3
	Total	198.5	198.7
Sewage Sludge + Lime	Spoil	109	102
	Litter	21.5	20.6
	Vegetation	19.9	33.9
	Total	150.4	156.5
Alginure + Lime	Spoil	136	121
	Litter	22.9	18.8
	Vegetation	7.4	20.3
	Total	166.3	160.1
Peat + Lime	Spoil	140	123
	Litter	25.6	21.4
	Vegetation	5.3	18.9
	Total	170.9	163.3
No Amendment + Lime	Spoil	111	100
	Litter	24.2	20.5
	Vegetation	7.0	13.8
	Total	142.2	134.3
No Amendment + No Lime	Spoil	7.6	53
	Litter	-	-
	Vegetation	-	-
	Total	7.6	53

Table 4.37 Total potassium in the system (kg ha^{-1}) 1984

		No Maintenance	Maintenance
Chicken Manure + Lime	Spoil	192	264
	Litter	16.9	17.4
	Vegetation	8.6	11.0
	Total	217.5	292.4
Sewage Sludge + Lime	Spoil	128	243
	Litter	10.4	11.8
	Vegetation	9.9	11.0
	Total	148.3	265.8
Alginure + Lime	Spoil	149	255
	Litter	12.7	14.4
	Vegetation	6.9	8.3
	Total	168.6	277.7
Peat + Lime	Spoil	132	225
	Litter	13.7	20.3
	Vegetation	5.6	8.7
	Total	151.3	254.0
No Amendment + Lime	Spoil	106	229
	Litter	13.6	12.6
	Vegetation	5.0	4.4
	Total	124.6	246.0
No Amendment + No Lime	Spoil	6.3	48.2
	Litter	-	-
	Vegetation	-	-
	Total	6.3	48.2

4.3.6 Mineralisation of nitrogen and phosphorus

The most important form of nitrogen for any vegetative system is the available nitrogen that is present in the root zone in a chemical form that is readily absorbed by plants (Scarsbrook 1965). This nitrogen can be derived from fertiliser, biological nitrogen fixation and mineralisation of organic nitrogen wastes, crop residues and soil organic matter. In most soils and climates, a significant proportion of soil organic nitrogen can be mineralised in a growing season. It has been reported that surface soils commonly contain between 0.08 and 0.4% total nitrogen (Bremner 1965a) the majority of which is in the organic form and if 1-3% of this is mineralised in a growing season (Bremner 1965b) then from 8-120 kg N/ha may become available.

In colliery spoil the total nitrogen levels mean very little as there is a significant amount of nitrogen in the organic component of the shale, 0.35% for Baads Colliery. Although this "fossil nitrogen" may be released on weathering, the rate at which this occurs is so low, except under extremely acid conditions, that the amount of nitrogen that is plant available is usually deficient. The literature indicates that nitrogen mineralisation rates in geological materials are generally lower than those found in soils.

Power et al. (1974) found that exchangeable ammonium in exposed Paleocene shales was readily nitrified, but on incubation there was no net increase in inorganic nitrogen indicating very limited mineralisation.

The authors suggested that the organic nitrogen in these shales was relatively inert to biological decomposition.

The results from the experimental plots at the Baads Colliery have indicated that nitrogen availability was inhibiting the establishment of a self-sustaining ecosystem. Therefore incubations were established to determine the quantity and rate of nitrogen mineralised in the colliery spoil from each of the experimental plots. The mineralisation of phosphorus and potassium were measured at the same time.

As this was a microbiologically mediated process, the amount of carbon turned over during the same period was also measured. The results in Table 4.38 show the amounts of carbon and nitrogen mineralised over a ten week incubation for the spoils sampled in 1983 and 1984. For all the treatments, large amounts carbon were turned over in comparison to nitrogen, and this is reflected by the high values of the carbon:nitrogen ratios. There was a large degree of variation in the amounts of carbon and nitrogen mineralised within each treatment, but the levels produced for the two years were similar indicating that there was no increase in the amount of organic nitrogen available for mineralisation within the spoil. Within any one year there was no significant difference between treatments for the limed plots which again suggests similar levels of mineralisable organic matter within the spoil.

Table 4.38 Carbon and nitrogen mineralised over 10 weeks

Treatment	Amount of element mineralised (mg/kg) mean and (standard deviation)				
		1983		1984	
Chicken Manure + Lime	C	1907	(312)	1940	(647)
	N	33.3	(13.8)	34.0	(15.7)
	C:N	57		57	
Sewage Sludge + Lime	C	1501	(205)	1784	(342)
	N	19.4	(5.9)	24.1	(7.0)
	C:N	77		74	
Alginure + Lime	C	1586	(137)	1431	(310)
	N	17.0	(7.5)	29.5	(13.6)
	C:N	93		49	
Peat + Lime	C	1650	(51)	1873	(927)
	N	18.0	(6.4)	23.0	(11.9)
	C:N	92		82	
No Amendment + Lime	C	1128	(498)	1508	(226)
	N	22.8	(8.3)	31.6	(14.5)
	C:N	49		48	
No Amendment + No Lime	C	143	(27)	160	(51)
	N	4	(3.4)	1.5	(2.8)
	C:N	36		133	

It would appear from these observations that there was no residual effect on mineralisation from the organic amendments that were incorporated at the onset of the trial, four years previously. The majority of dead vegetative matter from the previous years was found to be lying on the surface of the spoil with only very poor incorporation. This poor incorporation may be happening at a similar rate in each of the treatment plots resulting in similar levels of biodegradable organic matter within the spoil which would explain the similarity in mineralisation results. Any differences between treatments would therefore be found in the build-up of dead litter. In the unlimed plots there was significantly less carbon and nitrogen mineralised, and this is likely to be due to the extremely low pH (2.5-3.0) rather than the lack of degradable organic matter. However Reeder and Berg (1977) observed very low levels of nitrogen mineralisation on unvegetated fresh spoil that had a pH of 8.

Comparison of the results from this experiment with those of previous studies is difficult due to the variety of methods used. For example Reeder and Berg (1977), Palmer and Chadwick (1985) and Fyles and McGill (1987) all used air-dried spoil, whereas in this study fresh spoil was used. Similarly there are a number of incubation practices that have been used, such as whether the incubation was carried out under aerobic or anaerobic (waterlogged) conditions. The temperature of incubation is also very important. Some studies pre-leach the material with salt solutions to remove initial levels of inorganic nitrogen, while others incorporate vermiculite to improve leachability and aeration. The use of suction to remove excess water or leaching solution has been employed and also the addition of calcium carbonate or nutrient solution during the incubation. All these variables may have some effect on the mineralisation processes occurring within the soil/spoil. Despite these variations however it has usually been the case that far more carbon than nitrogen is released in this type of incubation. Even though the levels of nitrogen measured were low, they may represent the most important pool of nitrogen available to the plants. Palmer and Chadwick (1985) found that mineralisable nitrogen was the fraction most highly correlated with herbage nitrogen.

During the second incubation (1984) the levels of nitrogen mineralised were measured during the ten week period allowing cumulative plots to be calculated. For two of the samples it was observed that the majority of the inorganic nitrogen remained in the ammonium form (Figure 4.11) and it was noted that the pH of the spoil for these samples was roughly 4.5. It would appear that either the pH, or a factor resulting from this lower pH inhibited the nitrifying process within these spoil samples.

Figure 4.11 Nitrogen mineralisation curve for colliery spoil with pH below 5, showing inhibition of the nitrifying process.

Figure 4.12 Nitrogen mineralisation curve for colliery spoil with pH above 5.

Figure 4.11

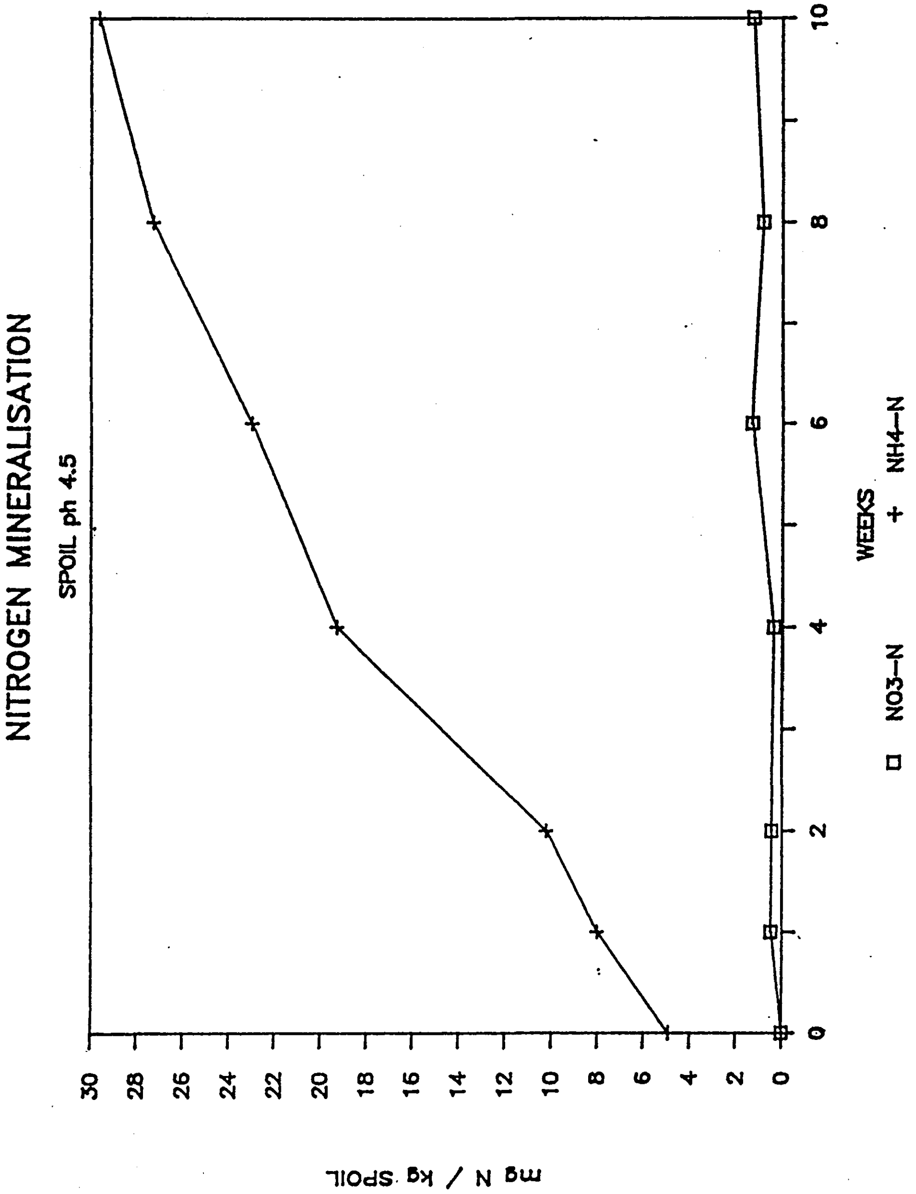
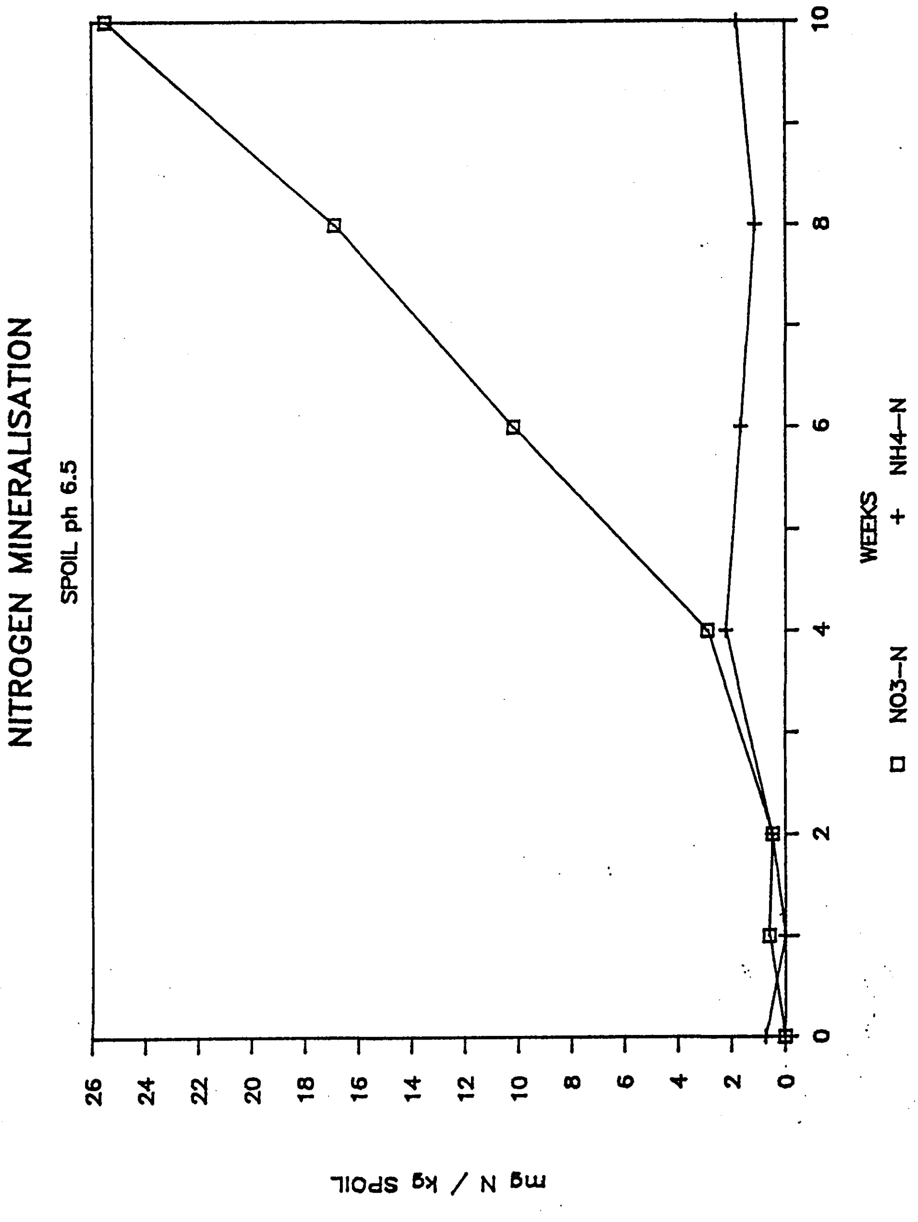

NITROGEN MINERALISATION
SPOIL ph 4.5
mg N / kg SPOIL
30
28
26
24
22
20
18
16
14
12
10
8
6
4
2
0
0
2
4
6
8
10
WEEKS
□ NO3—N
+ NH4—N

Figure 4.12


NITROGEN MINERALISATION
SPOIL ph 6.5
mg N / Kg SPOIL
0
2
4
6
8
10
12
14
16
18
20
22
24
26
WEEKS
0
2
4
6
8
10
□ NO3–N
+ NH4–N

In most cases however the mineralisation sequence followed the pattern found in Figure 4.12. The levels of ammonium remained low throughout the incubation, whereas the nitrate levels after low initial production became mineralised at a steady rate after about four weeks. This initial immobilisation of nitrogen coincided with the initial flush in carbon production observed (Figure 3.4) that was caused by the disturbance on sampling and handling the spoil. The carbon release also became linear after week 4. Therefore it was possible to estimate the rate of release of carbon and nitrogen once equilibrium had been reached.

Stanford and Smith (1972) developed an incubation approach to define the mineralisable soil nitrogen pool. This approach involves estimating nitrogen mineralised over an extended period of time with the inorganic nitrogen being removed at various times during the incubation. Cumulative nitrogen production is then plotted against the square root of time. The nitrogen mineralisation potential, N_0, is assumed to follow first order kinetics and is estimated as:

$$\text{Log } (N_0 - N_t) = \text{Log } N_0 - Kt/2.303$$

Their initial work on 39 widely differing soils gives an average K of $5.4 \pm 0.9\%$ of the total nitrogen mineralised per week, and an average N_0 (as percentage of total soil N) of $18.4 \pm 7.9\%$. They concluded that K and N_0 are parameters that can be used to give quantitative estimates of nitrogen mineralisation in soils.

However, as in the study of Fyles and McGill (1987), the results for the material used in this experiment did not follow first order kinetics, so the values of potentially mineralisable nitrogen, N_0, could not be measured. The zero order rate constants for carbon and nitrogen are therefore presented in Table 4.39. These again show a much higher release of carbon than nitrogen, with no real significant difference between treatments. The carbon:nitrogen ratios were lower than those in Table 4.38, as would be expected when the effect of initial carbon flush and nitrogen immobilisation have been removed. The findings of this study, like those of Wilson and Stewart (1955), Reeder and Berg (1977) and Williams and Cooper (1976), indicate that net nitrogen mineralisation was generally low in geologic materials, and that a small proportion of the total nitrogen is potentially mineralisable.

In contrast the levels of microbial activity were high in these materials which leads to the question of why there was this apparent lack of nitrogen mineralisation. Only net mineralisation was measured, so it was not possible to evaluate the relative magnitudes of concurrent immobilisation and mineralisation processes. The high carbon:nitrogen ratios of the shales could lead to microbial immobilisation of the nitrogen.

Table 4.39 Zero Order rate constants for C and N turnover during incubation at 25°C

Treatment	Zero Order rate constants		
	mg CO_2-C released per kg spoil/week	mg N released per kg spoil/week	C:N
Chicken Manure + Lime	146.4	3.8	39
Sewage Sludge + Lime	127.5	2.72	47
Alginure + Lime	101.4	3.29	31
Peat + Lime	143.6	2.48	58
No Amendment + Lime	102.0	3.46	29
No Amendment + No Lime	16.5	0.68	24

Another possibility could be that a fraction of the mineralised ammonium may be fixed within the structures of the secondary silicate minerals found in shale materials.

The levels of phosphorus mineralised (Table 4.40) were very low, 0-3 mg P/kg, for all the treatments except chicken manure. This treatment gave reasonable levels in both years, mean of 12-16 mg P/kg, but this was highly variable between plots.

The levels of extractable potassium measured at each stage during the incubations varied to such an extent that no conclusions could be drawn on the levels mineralised. Potassium availability in coal spoil is dominated to such an extent by the shale material itself that any small changes derived from the breakdown of organic matter may not be observed.

Table 4.40 Phosphorus mineralised over 10 weeks

	Amount of P mineralised (mg/kg) mean and (standard deviation)	
	1983	1984
Chicken Manure + Lime	12.5 (8.6)	15.7 (9.3)
Sewage Sludge + Lime	3.0 (1.2)	2.2 (1.0)
Alginure + Lime	1.2 (0.6)	0.9 (0.6)
Peat + Lime	2.0 (0.5)	2.3 (2.1)
No Amendment + Lime	1.6 (1.4)	1.1 (0.6)
No Amendment + No Lime	0.17 (0.09)	-0.04 (0.17)

4.3.7 Fertiliser response

The deficiency of the major nutrients nitrogen and phosphorus, and to a lesser extent potassium, is a universal problem encountered in the reclamation of derelict land. This is frequently remedied by the application of substantial amounts of fertiliser, either inorganic or organic, which can produce immediate and effective results. However, if no further maintenance programme is established, then the scheme usually fails, and this is almost always due to a shortage of nitrogen. Bloomfield, Handley and Bradshaw (1982) noted that if nitrogen was applied, growth would recommence, but would stop again if further nitrogen was not given.

The evidence from the levels of extractable nitrogen, phosphorus and potassium, and the rates of turnover of carbon and nitrogen suggested that nitrogen and phosphorus were very deficient in the spoils at the experimental site at Baads Colliery. A fertiliser respnse trial was established using two levels of nitrogen, phosphorus and potassium both individually and in combination with each other. The effect of these treatments were compared against a control plot that had received no fertiliser. The results presented in Table 4.41 show the vegetation yields and nutrient contents for each of the treatments. The vegetation yield increased significantly ($p<0.05$) only when 100 kg N/ha was applied either on its own or in combination. No effect on vegetation was measured by additions of phosphorus or potassium alone, or by 50 kg N/ha.

Table 4.41 Fertiliser response plots - herbage yield and NPK content

N	P	K	Herbage yield*	Herbage content		
	kg/ha		t/ha	%		
				N	P	K
0	0	0	1.7^{a}	1.16	0.16	0.46
50	0	0	1.6^{a}	1.17	0.18	1.04
100	0	0	3.3^{b}	1.37	0.19	1.16
0	30	0	1.2^{a}	1.53	0.22	0.85
0	60	0	1.2^{a}	1.44	0.32	1.09
0	0	30	1.8^{a}	1.11	0.20	0.73
0	0	60	1.3^{a}	1.34	0.20	0.76
50	30	30	1.3^{a}	1.29	0.24	0.85
100	60	60	2.6^{b}	1.50	0.30	1.17

* Values with the same letter following are not significantly different at the 5% level using a Fisher LSD test.

Although there was an increase in yield at the higher nitrogen application rate, this level of production was not substantial and was less than would be expected for a poorly productive temperate ecosystem (Bradshaw 1983). A comparison of this and the fact that there was no apparent improvement in the nitrogen content of the sward indicated that even the addition of 100 kg N/ha was not enough to alleviate the nitrogen deficiency found in this spoil.

The effects of the phosphorus additions were less clear. Fitter and Bradshaw (1974) and Doubleday and Jones (1977) both showed an increase in vegetation yield with added phosphorus. Pulford and Duncan (1978) measured only a slight decrease in yield in two spoils, and no effect in a third spoil when no phosphate was added in a pot trial. In this experiment there was no yield increase with phosphorus additions, but in the plots receiving 100 kg N/ha alone or with phosphate and potassium, the phosphorus content of the grass did not decline, implying that at this low level of grass production phosphate was not limiting to growth. However, if enough nitrogen were added to improve the yield more substantially (ie. >5 t/ha), then there may be a requirement to improve the phosphate availability within the spoil.

There was no apparent effect from the potassium additions on the herbage yield or nutrient content as the background levels found in the spoil material overshadowed the relatively small quantities added by fertiliser.

Although the majority of the treatments used in this trial had no effect on vegetation yield or nutrient supplying power of the spoil, there was a marked visual improvement in the grass sward which appeared much greener and healthier. However due to the lack of improvement in the spoil conditions it seems unlikely that this healthier appearance will continue beyond the season of application.

CHAPTER 5

GENERAL CONCLUSIONS

The direct measurement of organic matter build-up in unburnt colliery shale was hindered by interference from the background levels of carbonaceous material associated with the shale. None of the standard chemical techniques used; loss on ignition, peroxidation, Walkley and Black or Tinsley methods were able to distinguish the background material from any recently accumulated organic matter due to reclamation practices.

However the rate of CO_2 evolution from soils measured under laboratory conditions could be used as an index of organic matter available for microbial activity and breakdown (Waksman and Starkley 1924). Fyles et al. (1985) have shown that CO_2 evolution on reclaimed minespoil was similar to that from soil from a nearby native grassland, but that the soil had a higher total organic matter and nitrogen levels. This would indicate that the soil had a large pool of organic residues which were resistant to microbial degradation. This is consistent with the theory of active and passive fractions of organic nitrogen in soil which is of importance to the concept of carbon and nitrogen cycling.

The reclaimed plots at Baads had similar CO_2 evolution rates to soils with an organic matter content of about 2 to 3 percent. Therefore they probably have similar levels of degradable organic matter, which is the portion of importance to nutrient cycling, but may not have attained the same degree of resistant material which is involved in spoil structure development.

These low levels of organic matter accumulation were similar for all the amended plots receiving lime, and this was attributed to the poor incorporation of any dead vegetation. The resultant build-up of surface litter was different for each treatment and reflected the success of each treatment to stimulate early growth.

Spoil extractions of the three major nutrients showed that at this stage in the reclamation scheme the levels of available nitrogen and phosphorus were extremely low. Potassium appeared to be in adequate supply, being released from shale by weathering. The levels of mineralisable nitrogen and phosphorus in the spoil were also very poor and the observed trend of yield decline with age was probably due to nutrient deficiency, especially of nitrogen. Maintenance fertiliser additions resulted in a quick response, in particular when higher levels of nitrogen were applied. Phosphorus and potassium when applied without nitrogen gave no improved grass yield.

Nutrient budget studies showed that the treatments used so far had led only to the build-up of a small nutrient capital. This appeared to have increased between 1983 and 1984, but at the rate observed, would take 10 years for sufficient nitrogen to accumulate that would sustain a self-supporting system. This was further complicated by the fact that the majority of the accumulated nitrogen was tied up in the organic litter which was relatively unavailable for breakdown and utilisation.

The experimental plots would therefore benefit in two ways from the incorporation of this litter layer. The increase in spoil organic matter would help develop the spoil structure and further improve water relations, cation exchange and bulk density. The incorporated organic matter would also become more susceptible to microbial attack and so a greater percentage of the nutrient capital established would become available for cycling. Incorporation could be achieved by ploughing in the litter material, but this may lead to other problems such as acid regeneration by exposing unweathered material. A more ecological solution would be the introduction of an earthworm population that would not only incorporate the organic matter naturally, but would also improve the physical nature of the spoil as a result of their burrowing.

These trials are typical of most reclamation schemes in that unless a sufficient nutrient capital has been established, vegetation regression develops if maintenance dressings of fertiliser, especially nitrogen, are not applied. Fertiliser additions result in a very expensive aftercare programme, and the results are generally shortlived without any obvious spoil improvement. The use of organic amendments, particularly manures, provides a cheaper alternative to fertilisers in the initial stages of reclamation, but still results in deficiency problems in the long-term.

The long-term supply and accumulation of nitrogen can be achieved by the use of legumes in the reclamation seed mix. Legumes have been shown to increase nitrogen availability in colliery spoil which can be utilised by the companion grass (Jefferies et al. 1981). In the majority of cases, agricultural legumes such as white clover (Trifolium repens) are used which require careful management.

Legumes are generally susceptible to high levels of inorganic nitrogen, therefore the initial stages of reclamation have to be modified. It is relatively simple to stimulate growth and provide a good healthy vegetation cover by the addition of high levels of manure or fertiliser, but this invariably kills off the legume component of the seed mix. This initial good growth may have to be sacrificed to allow the legumes to develop and build up the nitrogen availability slowly.

The nitrogen fixing ability of the legumes is heavily dependant on the availability of phosphate (Palmer and Iverson 1983), so this should be supplied at seeding where necessary.

Once established, sward management is important as the legumes can be phased out by competitive exclusion from the companion grass. Grass cutting may be required to prevent the legumes from being overshadowed. This litter would also have a higher nutrient content than if left to die back at the end of the season, so should be more readily decomposed.

If a minimum of aftercare was required, then a more hardy, competitive legume should be employed, and further research is required to find the species best suited to this task.

Although the use of phosphate fertiliser and legumes may provide long-term successes in vegetation yield, the ensuing litter has to be incorporated to develop the spoil and stimulative nutrient cycling. If not the nutritional benefits from the legumes will be tied up in the litter mat, which may eventually stifle out the legumes themselves and result in the degeneration of the reclamation scheme.

The use of legumes in conjunction with organic manures may provide a more economic and more persistent solution to the problem of supplying sufficient nitrogen both in the short-term and the long-term.

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