THE INFLUENCE OF LAND MANAGEMENT ON UPLAND WATER QUALITY
NOTABLY THE PRODUCTION OF SOLUBLE COLOUR IN SUPPLY.

DAWN STEPHANIE JEAN MARTIN

SUBMITTED IN ACCORDANCE WITH THE REQUIREMENTS FOR THE DEGREE OF
DOCTOR OF PHILOSOPHY.

The University of Leeds School of Geography.
University of Leeds
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ABSTRACT

Colour in upland water supplies is increasing, its levels have been related to droughts in 1976 and 1984, the highest level occurring in 1985. Records from treatment works indicate that colour varies between catchments which suggests that drought and its subsequent soil moisture deficits, is not the only causal factor in colour production.

Research has shown that colour levels are related to both the physical and management characteristics of moorland. The most significant physical factor being the area of deep peat per catchment, as this represents the source of humic and fulvic acids which give rise to colour flows. Within these peat catchments, variations in colour level occur that cannot be explained by peat alone, leading to the conclusion that moorland management strategies may also be responsible. Strategies studied included burning, ditching and liming, and consideration was given to the suggestion that liming may reduce the amount of colour in raw waters.

These practices were found to increase soluble colour and in turn, levels of iron and aluminium in supply. Burning and ditching processes are linked to reductions in soil moisture, aerating soil conditions and in turn increasing levels of organic acids through decomposition. Liming increases pH and leads to increased decomposition, albeit by a slightly different set of processes, but has the same result.

Several research sites in North Yorkshire were used, the main ones being Howstean and Inmoor catchments, Scar House reservoir, in Upper Nidderdale, an area where discoloration had already been identified on a catchment scale and sites at the Washburn valley (Fewston and Thruscross reservoirs); Glasedale, North Yorkshire Moors and Gunnerside Moor, Upper Swaledale. Research involved large and small scale field and laboratory work, including extensive water sampling; isolation of four large peat blocks subsequently drained and treated by burning and liming to assess the effects on soil moisture and colour production; and peat sampling in the form of cores, some of which were treated, burned or limed and then leached using rainfall simulation. Resulting samples were analysed for water quality parameters, including colour, aluminium and iron.

Results have enabled those processes which potentially produce colour and the factors governing its magnitude to be addressed; allowing management strategies for its reduction to be formulated. Emphasis is placed on the need for good moorland management of heather, burning at a reduced temperature thereby minimising the effect on colour production; and the need to restrict or avoid drainage, so keeping soil moisture deficits to a minimum. Finally, it is suggested that management of colour by large scale liming is both inappropriate and ineffective as it appears to increase, rather than decrease, colour.
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The Nickerson Group Estate owners southside of Howstean.

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Finally I must thank my parents for all their support over the years of my "education" culminating in the production of this thesis, which I dedicate to them.
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CHAPTER ONE

INTRODUCTION AND BACKGROUND INFORMATION

1.0. THE PROBLEM OF COLOUR IN SUPPLY

1.0.0. THE PROBLEM AND ITS BACKGROUND

Wherever raw water is gathered from upland peat areas it is coloured to some degree and although some Water Companies can deal effectively with this problem, others are experiencing increasing difficulty in its effective extraction in their treatment works, both at an acceptable cost and in meeting E.C. quality standards. Currently, the Severn and Trent Water, North West Water and Northumbrian Water companies have few problems with colour and find no pronounced upward trend in colour although they do recognise seasonal fluctuations. However, other Water Companies have noted an upward trend, as well as seasonal
fluctuations. Welsh Water, Dumfries and Galloway Water Department and Yorkshire Water have noted a significant upward trend, resulting in treatment problems. (Buckley, Crabtree, Hall, Wright, Parr, Edwards 1987).

As Yorkshire Water seems most affected by increasing colour levels nearly all of this work and discussion is based upon this region. The nature of the problem however seems to be common to all affected regions, and therefore it is felt that the work is relevant also to them.

Yorkshire Water has 88 direct supply reservoirs located in areas of Millstone Grit rocks in the head-waters of the rivers Aire, Calder, Don, Ure and Wharfe. In 50% of these reservoirs the potable supply is derived from upland surface catchments, the vast majority of which lie in the Pennines. The gathering grounds of the reservoirs cover 52,300 ha of which a third is owned by Yorkshire Water (mostly let to tenants). Land use comprises of:

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<td>Pasture/Agriculture</td>
<td>28%</td>
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<td>Woodland</td>
<td>4%</td>
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Much of the moorland is covered by thick peat deposits of up to 5m thick, and is subjected to an annual average rainfall which rises to over 1500mm along the main watershed of the Pennines. These peat deposits contain
large amounts of organic acids (humic and fulvic) which dissolve in the runoff from catchments and discolour the water, resembling weak tea. The resulting water in the reservoirs is not only discoloured but also soft (low in Calcium Carbonate), oligotrophic and acidic. Acidity is due to rainfall of pH 4.2 to 4.5 in the region and to the dissolved organic acids. Such water by its very nature, is an excellent solvent and readily dissolves the trace metals present in the soil, producing a water containing significant quantities of aluminium, iron and manganese. In the past such waters have been treatable because levels of colour and dissolved metals have been relatively low. Over the last fourteen years however, levels of colour and associated metals have been increasing and are currently causing treatment problems, an increasing number of consumer complaints and a failure to meet EC water quality standards.

1.0.1. TRENDS IN WATER DISCOLORATION

The extent of the discoloration and level of metals present in the runoff, varies considerably from catchment to catchment. Many factors appear to affect this but the mechanics are not well understood, although it has been suggested that land usage is significant (discussed in
Fig. 1.1

THORNTON MOOR WTW.
RAW WATER COLOUR.
SKETCH GRAPH OF MONTHLY MEANS.

True Colour ABM
Fig. 1.2

RAMSDEN WOOD RAW WATER
COLOUR 1976 – 85

TRUE COLOUR (HAZEN)

MAX

AVE

Fig. 1.3

RAMSDEN WOOD COAGULANT
COSTS 1976 – 85
Fig. 1.4 -

RAW WATER TRUE COLOUR: HOLME VALLEY RESERVOIRS.

HOLMEBRIDGE WTW

YEAR

BROWNHILL WTW

YEAR
a later section). Discoloration also shows a strong seasonal variation in that it is always greatest between October and March. Rapid increases in colour are observed in the late Autumn when the first flushes of heavy rainfall extract the highest levels of colour and flow into relatively empty reservoirs minimising 'dilution'. This seasonal effect suggests that the extraction of colour from the peat deposits is related to soil moisture levels although other factors may be involved. Such spatial and annual trends have always been present but the maximum colour values involved are increasing.

These increases are seen as a more recent and problematic trend in temporal colour values. In some areas, the degree of discoloration during the Autumn of 1985 reached levels higher than ever previously recorded, the reasons for this are unclear but are currently being researched. It has been suggested that this problem is related to the 1984 drought when the peat deposits lost much of their water content, resulting in colour generation, with the full extraction of the colour taking place the following Autumn. It has also been claimed that this effect was observed during the Autumn of 1977 following the droughts of 1975 and 1976. More disturbingly it has been reported that the raw water colour observed after the Autumn of 1977 has never returned to pre-1976 levels and variability in colour levels has also increased.
Examples of increases in discoloration are numerous but not all reservoirs exhibit the same trends. Thornton Moor reservoir, west of Bradford, exhibits the seasonal cycle clearly and shows a sharp rise in the Autumn of 1977, a year after the severe droughts of 1975/76. Increased variability and colour levels are also exhibited, the highest colour being recorded in the Autumn of 1985, see figure 1.1. Levels of discoloration have continued to fluctuate, means (and maxima) for the years 1987 to 1992 are: - 4.24 (8.8), 3.59 (5.88), 2.44 (8.32), 1.80 (2.82), 1.92 (3.62) and 2.00 (3.40) in Abm⁻¹. Maximum colour recorded for 1989 when conditions were unusually dry are of similar magnitude to those recorded in 1984 after the drought.

An example of a dramatic increase in raw water colour in the Yorkshire Region has been observed at Ramsden Wood reservoir which feeds Thrum Hall treatment works. Figure 1.2. shows that a 15-fold increase took place in the annual maximum raw water colour between 1976 and 1985 (up to 11.5 Abm⁻¹) and a 4-fold increase in the annual average raw water colour from 1979 to 1985 (to 7.5 Abm⁻¹). Maximum colour values have remained elevated, the maximum for 1987 increasing beyond that previously recorded (188 Hazen), data beyond 1987 is not available. (All figures beyond 1986 have been provided by J. Warne, Yorkshire Water, personal communication.)
Comparison of two neighbouring reservoirs, Holmebridge and Brownhill, shows how colour varies from reservoir to reservoir. These are both situated at the head of the river Holme, south of Huddersfield yet they exhibit different colour values, raw water from Holmebridge being more highly coloured, see figure 1.4. These differences indicate that the mechanism behind colour generation is not a simple one and that other factors maybe involved. Fluctuations of this nature have continued to date.

Many people have supported the theory that the high levels of colour are related to the 1984 drought and have commented on similar phenomena observed following the 1975 and 1976 droughts and that these effects appear, in some cases, to have become irreversible. These include several Water Authorities/Companies, see Buckley et al (1981), Parr and Edwards (1987).

1.0.2. POSSIBLE CAUSES OF DISCOLORATION

Although no precise mechanism for the generation of discoloured water is currently recognised, it is accepted that the dissolution of humic and fulvic acids amounts to the chemical erosion of peats and it is suspected that there may be an inter-relationship between this and the mechanical erosion of peats.
Causes of both chemical and mechanical erosion have been identified, as also have the main environmental changes in the Pennines that could impact on water quality. These are:

i) CLIMATE
   Natural variations, with man induced ones probably becoming evident in the future.

ii) GRIPPING
    Moorland drainage for Grouse or sheep management.

iii) FIRE
    Controlled heather burning and the more damaging, accidental fires.

iv) GRAZING
    The density of sheep grazing affects the regeneration of vegetation and hence can influence the rate of peat erosion.

v) AGRICULTURAL IMPROVEMENT
    Involving drainage and the application of lime, fertilisers and pesticides. There is also the possibility in the future of land being taken out of cultivation.

vi) FORESTRY
    Including pre-planting, land preparation and harvesting.

vii) RECREATION
    Footpath erosion.
viii) AIR POLLUTION

The Pennines have been subject to atmospheric pollution since the beginning of the industrial revolution.

ix) MOORLAND RESTORATION

Experiments are in progress to revegetate bare, eroded peat which if practised on a large scale, could have long term benefits for water quality and run-off patterns.

(EDWARDS 1987)

These possible causes divide into two interrelating processes.

i) "Natural" Processes. Mainly Climatic and Hydrological

and


Both processes are capable of producing similar environmental effects; such as changes in soil moisture, pH and rates of decomposition, though the scale and spatial and temporal effects differ.
Natural effects are usually large scale and occur over wide areas, (albeit to differing degrees, dependent on soil moisture). Such effects are however, relatively infrequent as in the case the 1976 drought, which had a calculated recurrence interval of 1000 years. Although climatic change may alter such recurrence intervals the effects of drought are long lasting and irreversible.

Conversely, anthropogenic effects are generally small scale by comparison and may be limited to individual catchments e.g., ditching and liming; or to parts of catchments e.g., burning. Whilst effects may be long term, in the case of ditching or short term as with liming and burning, they are created much more frequently and may be more severe, albeit over a smaller area.

As stated in Section 2.0. the aims of this research are concerned with the Anthropogenic effects.

1.0.3. THE NATURE OF COLOUR IN WATER

Humic substances may be defined as 'a general category of naturally occurring, biogenic and heterogeneous organic substances which may be generally characterised as being yellow to black in colour, of high molecular weight and refractory' (Aiken et al. 1985). 'These substances cannot be defined in terms of structure or of function because they do not belong to any unique chemical entity (as do
proteins and polysaccharides) nor do they have any unique biochemical function. They are therefore defined operationally in terms of solubilities in aqueous acids and bases. Humic acids are combined in the fraction of humic substances precipitated at pH1 from solution in aqueous alkali. Fulvic acids remain soluble in water at all pH values, and the Humin components are insoluble in water at any pH value.' (Hayes, 1987).

Thus, humic substances split into three main groups: Fulvic acid, Humic acid and Humin which represent the complex mixture of molecules of various sizes and shapes that are classed as humic substances. At present, no precise chemical characterization of the substances in the three groups exists. Instead, groups are defined by certain physical and chemical characteristics of humic molecules, for example molecular weight or other characteristics such as those in Table 1.1, this table also presents some useful definitions and also the properties of humic substances.

Many established techniques are working towards the characterization of humic substances, which provide valuable information regarding their physical and chemical structure. Such techniques are mentioned at length by Schnitzer and Khan (1978), and Hayes (1987), an example and the knowledge gained from it, are given below.
Table 1.1

General Properties of Humus and Associated Effects in the Soil.

**STEVENSON, F.J. (1982).**

<table>
<thead>
<tr>
<th>Property</th>
<th>Remarks</th>
<th>Effect of Soil</th>
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<tbody>
<tr>
<td>Color</td>
<td>The typical dark color of many soils is caused by organic matter</td>
<td>May facilitate warming</td>
</tr>
<tr>
<td>Water retention</td>
<td>Organic matter can hold up to 20 times its weight in water</td>
<td>Helps prevent drying and shrinking. May significantly improve the moisture-retaining properties of sandy soils</td>
</tr>
<tr>
<td>Combination with clay minerals</td>
<td>Cements soil particles into structural units called aggregates</td>
<td>Permits exchange of gases Stabilizes structure Increases permeability</td>
</tr>
<tr>
<td>Chelation</td>
<td>Forms stable complexes with Cu++, Mn++, Zn++, and other polyvalent cations</td>
<td>May enhance the availability of micronutrients to higher plants</td>
</tr>
<tr>
<td>Solubility in water</td>
<td>Insolubility of organic matter is because of its association with clay. Also, salts of divalent and trivalent cations with organic matter are insoluble. Isolated organic matter is partly soluble in water</td>
<td>Little organic matter is lost by leaching</td>
</tr>
<tr>
<td>Buffer action</td>
<td>Organic matter exhibits buffering in slightly acid, neutral, and alkaline ranges</td>
<td>Helps to maintain a uniform reaction in the soil</td>
</tr>
<tr>
<td>Cation exchange</td>
<td>Total acidities of isolated fractions of humus range from 300 to 1400 meq/100 g</td>
<td>May increase the cation exchange capacity (CEC) of the soil. From 20 to 70% of the CEC of many soils (e.g., Mollisols) is caused by organic matter</td>
</tr>
<tr>
<td>Mineralization</td>
<td>Decomposition of organic matter yields CO₂, NH₄⁺, NO₃⁻, PO₄³⁻, and SO₄²⁻</td>
<td>A source of nutrient elements for plant growth</td>
</tr>
<tr>
<td>Combines with organic molecules</td>
<td>Affects bioactivity, persistence and biodegradability of pesticides</td>
<td>Modifies application rate of pesticides for effective control</td>
</tr>
</tbody>
</table>

**Terms and Definitions**

- **Humus** (Decomposition products of organic residues)
- **Nonhumic substances** (Known classes of organic compounds)
- **Humic substances** (Pigmented polymers)

<table>
<thead>
<tr>
<th>Term</th>
<th>Definition</th>
</tr>
</thead>
<tbody>
<tr>
<td>Organic residues</td>
<td>Undecayed plant and animal tissues and their partial decomposition products</td>
</tr>
<tr>
<td>Soil biomass</td>
<td>Organic matter present as live microbial tissue</td>
</tr>
<tr>
<td>Humus</td>
<td>Total of the organic compounds in soil exclusive of undecayed plant and animal tissues, their &quot;partial decomposition&quot; products, and the soil biomass</td>
</tr>
<tr>
<td>Soil organic matter</td>
<td>Same as humus</td>
</tr>
<tr>
<td>Humic substances</td>
<td>A series of relatively high-molecular-weight, brown to black colored substances formed by secondary synthesis reactions. The term is used as a generic name to describe the colored material of its fractions obtained on the basis of solubility characteristics. These materials are distinctive to the soil (or sediment) environment in that they are dissimilar to the biopolymers of microorganisms and higher plant (including fungal)</td>
</tr>
<tr>
<td>Nonhumic substances</td>
<td>Compounds belonging to known classes of biochemistry, such as amino acids, carbohydrates, fats, waxes, resins, organic acids, etc. Humus probably contains most, if not all, of the biochemical compounds synthesized by living organisms</td>
</tr>
<tr>
<td>Humus</td>
<td>The ash insoluble fraction of soil organic matter or humus</td>
</tr>
<tr>
<td>Humic acid</td>
<td>The dark-colored organic material which can be extracted from soil by various reagents and which is insoluble in dilute acid</td>
</tr>
<tr>
<td>Fulvic acid</td>
<td>The colored material which remains in solution after removal of humic acid by acidification</td>
</tr>
<tr>
<td>Humus melanolic acid</td>
<td>Alcohol soluble portion of humic acid</td>
</tr>
</tbody>
</table>
Nuclear Magnetic Resonance Spectrometry (NMR) observes the magnetic spin momentum of nuclei of certain atoms by placing them in a magnetic field and exciting them with radio waves. This causes energy transitions to occur, which are displayed as spectra. Such spectra provide valuable information regarding the immediate chemical environment of the atom under study. Using the technique of NMR the spectra for humic substances in river water were observed. Spectra for humic and fulvic acid were similar in pattern, displaying certain chemical groups common to both; these groups include, aliphatic groups, ketones, aromatic groups (especially phenols and phenolic groups), polysaccharides, carbonyl groups and carboxyl groups. Some differences in the spectra do occur though, noticeably in the region of the spectra corresponding to phenolic and carbonyl groups. Humic acid exhibits more phenolic groups. Studies have also compared different samples from rivers and lakes, revealing similar spectra, the only difference occurring in the phenolic and carbonyl regions of the spectra. These differences are thought to be related to differences in proportions of humic and fulvic acid.

NMR techniques reveal the chemical components that make up humic substances. To investigate the structure of such substances a technique involving the study of frictional coefficients is used. Calculation of the frictional ratio \( f/f_0 \) allows estimation of particle shapes. The method
compares the real frictional coefficient \((f)\) of a particle with the frictional coefficient of an unsolvated sphere of the same mass \((f_0)\). Such studies indicate that humic and fulvic acids are colloidal, consisting of long chain macromolecules which coil in a random fashion. Mutual repulsion by ionic species causes the coiled nature of such molecules to relax and leads to maximum expansion/volume of the particles. At higher molecular weights the frictional coefficient of particles increases, suggesting that branching occurs on the heavier humic acid molecules, (\(>10^5\) molecular weight). As a result they exhibit a denser structure owing to extensive branching.

The structural shape of humic and fulvic acids is also shown to be affected by the functional groups they contain and the chemical state of these groups. For example, structural properties vary with H\(^+\) ion concentration. Addition of H\(^+\) ions caused the reaction:

\[
\begin{align*}
\text{Phenolate groups} & \quad \text{------------ phenol} \\
\text{Carboxylate groups} & \quad \text{------------ carboxyl}
\end{align*}
\]

causing the molecule to shrink. When the pH of a humic acid solution is lowered to, or below pH 3.0, hydrogen ions associate with the negatively charged groups, allowing inter and intramolecular hydrogen bonding to take place and the macromolecules to shrink. As a consequence of this shrinking, water is expelled from the matrix by the reaction between H\(^+\) and OH\(^-\) which forms water and precipitation takes place. Fulvic acids do not
precipitate, however, because of the abundance of polar groups in their structures, which can be solvated. However, they can bond to precipitated humic acids by hydrogen bonding.

Divalent and polyvalent cations, added to humic substances in solution, have a similar effect to H+ ions which neutralizes two negative charges on the same or adjacent strands, this causes the macromolecular structure to shrink, water to be excluded from the matrix and precipitation to occur. Such reactions in mineral soils form bridges between negatively charged humic substances and negatively charged inorganic colloids.

As these reactions occur, drying takes place, causing important changes in the conformation of humic macromolecules, this may explain why humic acids and peats are difficult to rewet. During drying, the polar groups in the molecule orientate towards each other, either to facilitate hydrogen bonding, or coordination with inorganic cations. The hydrophobic nature of the dried materials suggests that these associations orientate towards the interiors of the macromolecules, rendering the exteriors hydrophobic. Conversely, addition of an alkali increases pH and causes the reverse reaction. This returns the outer layers of the coil to a hydrophillic state, allowing them to be rewetted. It is inferred that such reactions
can be related to drought and its effect on the rewetting potential of peat.

Other forces important in bonding humic substances in mineral soils are those of columbic attraction between humic substances and oxyhydroxides. Reactions include the interaction of humic substances with metal ions, metal oxides, metal hydroxides and more complex minerals to form metal-organic associations of widely differing chemical and biological stabilities and characteristics. Humic materials also contain per unit weight, relatively large numbers of oxygen rich functional groups (COOH, phenolic OH, C=O), through which they can attack and degrade soil minerals by complexing and dissolving metals, transporting these within soils and waters.

Interactions between humic substances and metal ions have been described as ion-exchange, surface adsorption, chelation, coagulation and peptization reactions, Mortensen (1963). Many researchers have investigated such reactions, see Schnitzer and Khan (1978), but only those reactions which are relevant are mentioned briefly below. Iron and aluminium are the most abundant metallic elements in the soil and as such their interaction with humic materials is of special concern. When Fe³⁺ and Al³⁺ are added to humic acid at low pH and the solutions are titrated with dilute base, precipitates are formed. These however, begin to dissolve as the titration proceeds and
the pH rises above 7.0. Van Dijk (1971) rationalises the above titration by the following mechanism: A proton is displaced from an acidic OH group of the humic acid at low pH; at higher pH, a proton dissociates itself from water which is covalently bonded to the metal ions and a hydroxy complex is formed which becomes more soluble, as more base is added. Schnitzer and Hansen (1970) have also shown that the stability constants of these complexes (FA and HA) increase with increased pH. The order of stabilities at pH 3.0 being:

Fe^{3+} > Al^{3+} > Cu^{2+} > Ni^{2+} > Co^{2+} > Pb^{2+} > Ca^{2+} > Zn^{2+} > Mn^{2+} > Mg^{2+}.

There is considerable uncertainty about the usefulness of such constants however, as not enough is known about the chemical structure of humic materials.

1.0.4. PHYSICAL AND CHEMICAL PROPERTIES OF HUMIC SUBSTANCES RELATED TO COLOURED WATER FROM UPLAND SOILS

Humic substances in peats associate mainly through hydrogen bonding and metal-organic complexation. This results from the high acidity and levels of iron and aluminium within these soils, predominant cations (H^+, Fe^{3+}, and Al^{3+}) neutralising the negative charge on the humic colloids. However, some of these bonding processes can be relatively weak, for example hydrogen bonding between fulvic and humic
acids, causing fulvic acids to be leached from the soil when rainfall is high and the weather warm. Humic acids are leached to a lesser extent due to their ability to precipitate. Other 'bonds' can be weakened by various processes, drying out or microbial activity for example. Polyvalent cations ($\text{Fe}^{3+}$, $\text{Al}^{3+}$) provide stronger bonding between the macromolecules than does hydrogen bonding. Raising the divalent/polyvalent cation status of the soil should therefore increase the amount of bonding, resulting in fewer humic substances being lost from the soil. However, such a mechanism relies on the availability of negatively charged inorganic colloids in the soil to enable the metal-organic complexes to bond to humic substances.

The greatest levels of discoloration occur some time after periods of drought. Hayes (1987), suggested that drying causes shrinkage of humic macromolecules leading to hydrophobic structures being orientated towards the exterior of the molecules, rendering them less soluble. He also suggests that drying affects the microbial population causing metabolism to decrease rapidly below a certain moisture content. When the moisture deficit decreases, rewetting is slow, humic substances returning to their previous dimensions.

Microbial activity has been shown by Birch (1958a, 1958b) to vary significantly between wet and dry cycles in peat, a burst of biological activity occurring after the
rewetting of dry organic matter. Increased activity leads both to the potential oxidation of humic acids to fulvic acids, and to the formation of fulvic acids, due to condensation of products produced during biological metabolism of organisms within the peat. Such products, fulvic acids and lower weight humic acids, are then open to removal by drainage waters if there are insufficient hydrogen or metal-organic bonding sites to hold the humic structures in the peat. Their removal resulting in discoloured stream water.

1.1 BACKGROUND TO MOORLAND MANAGEMENT BY BURNING. REVIEW OF THE LITERATURE

1.1.0 HEATHLAND MANAGEMENT

HISTORY.
Heathland management first became apparent in Bronze Age and Iron Age times in Western Europe. As a result of clearing, forest communities were replaced by simpler communities of Gramineae and Ericaceae. Cleared forest was colonised by these naturally occurring species which were already prevalent in glades in the forest, or above the tree line on the hills. On poor soils these communities developed into heaths, richer soils producing grassland. For these to be maintained, management was required to prevent the return of trees and shrubs. Management mainly
consisted of the introduction of domestic animals, but was supported by fire when necessary.

Changes of this kind continued during historical times, including felling of trees for fuel and construction which converted forest to heath; further felling took place in the fifteenth and sixteenth centuries to make charcoal (for smelting iron ore). As the English forest became depleted in Elizabethan times the practice of felling increased in Scotland, causing heathland to develop there.

As agricultural activity increased, poor management and over grazing caused heathlands to degenerate. For as long as cattle grazing predominated, the herbage was kept in productive condition and woody species and other pests such as _Pteridium aquilinum_ were kept in check. However, cattle were largely replaced by sheep, which had been driven into the uplands as a result of increasing arable activities in the valleys and which are highly selective grazers; hence these unwanted plant species flourished. It therefore became increasingly necessary to manage vegetation by burning as well as grazing. Firstly by the occasional and haphazard use of fire and from about 1800, by regular burning.

Burning was found to serve an additional purpose of promoting regeneration of heather, creating young nutritious shoots as well as suppressing unwanted species.
Shepherds adopted a ten-year burning rotation, aiming to burn one tenth of their total area of *Calluna* each year.

British hill sheep farming and its accompanying system of management by burning survives today, although it has declined in profitability over the 200 year period since its introduction.

In addition to management for sheep, management for Red Grouse became important in the latter part of the 19th Century. As areas of heathland increased, there was an increase in the populations of Red Grouse which feed largely on *Calluna*. Landowners began to appreciate the sporting value of this game bird and the income from the letting of shooting rights. This income supplemented the declining returns from sheep flocks and although both activities could be combined on heathland, increasing attention was paid to Grouse rearing from 1850 as there were greater financial incentives.

The preference for Grouse led to changes in heathland management. Gamekeepers discouraged shepherds from burning large tracts, in favour of small tracts. These provided a better habitat and better shooting as Grouse could be flushed more easily by beaters from the narrow, smaller stands. Burning smaller tracts resulted in a smaller proportion of *Calluna* being burnt each year and an increase in the areas of estates covered by ageing.
degenerate stands, which contain fewer young shoots and are therefore incapable of supporting large number of Grouse. In 1880, Grouse numbers had so drastically declined that it was urgently recommended that burning should return to a rotation of ten years.

This form of heathland management is still the generally accepted form of management today. Grouse moors represent a very valuable source of income and their management also benefits sheep farming to some extent. Britain is unique in its scale of Grouse shooting and at the same time it is the only country in which sheep farming on heathland has survived. It is possible therefore, that this form of heathland management is also unique to Britain, although burning rotations today have increased to 12-15 years intervals due to low manning levels.

TYPES OF MOORLAND MANAGEMENT

Two types of management exist today, burning and cropping. Burning is by far the most widespread, cropping has only recently been a suggested management practise as it is thought to have less profound ecological effects.

Burning involves the removal of a large proportion of the vegetation from narrow strips of moorland and it leaves approximately 15cm. of woody heather stem from which regeneration of young shoots can occur. The rotation of the burning cycle is between 12-15 years. This length of
rotation means that the heather stand is burnt either late in the building phase or early in the mature phase.

At these ages, heather has the greatest ability to regenerate vegetatively and the lower temperatures of burning which occur at these ages are sufficient to enhance germination of heather seed, rather than its destruction by higher temperatures. At these lower temperatures burning is restricted to the vegetation and to a small extent, the litter; therefore the seed bank in the litter and surface peat remains intact.

Narrow strips are burnt to provide a varied habitat for Red Grouse which require building or mature stands for nesting and pioneer stands, with young nutritious shoots, for food. These narrow strips are also preferred by Grouse as they like to be able to feed near the cover offered by building/mature heather.

Burning is restricted throughout Britain to a 'legal season' which now extends from the 1st October to the 15th April, having been extended in 1983. Previously the season ran from 1st November to 31st March with extensions possible until 15th April. The reform was essential as gamekeepers found it extremely difficult to meet the annual quota demanded by a 15 year rotation, within the shorter period. October and April provide the best burning conditions of the season but even with the increased
season, only a few days are generally suitable for burning and good organisation of resources is required to make full use of the available days. Shortage of such resources makes optimum management of moorland difficult and it is for these reasons that moorlands are now being poorly managed. The lack of resources, mainly manpower, has meant that the 15 year rotation cannot always be met and the problem is increasing. The increased number of warmer, wetter autumns and springs presents a further problem as burning is best carried out on the cold, frosty days which have become fewer. Consequently the ecological problems and changes associated with burning are increasing as the rotation in years increases. These problems and changes (physical, chemical, biological and ecological) are to be discussed later. Such events have lead to the introduction of an additional management practice, namely cropping which provides an alternative to burning late mature or degenerate heather.

Cropping (or cutting) is thought to be an acceptable alternative to burning, but it relies on the suitability of the moorland which must be accessible to machinery and relatively free from rocks. A double-chop forage harvester, or a turbo mower, is used to crop the heather and produce finely cut litter. Sometimes it is necessary to rake up and burn litter to ensure successful heather regeneration. The size of the Calluna strips treated is easily controlled and the method is less susceptible to
weather conditions. There seems to be no reason why this form of management should be restricted to the legal burning season and if it were not, more time per year would be available to achieve the 15 year rotation; but in the interests of Grouse management the breeding and fledging season should obviously be avoided. Cropping therefore appears to provide a good alternative to burning, but it still has associated problems, which are discussed later, mainly those of access and increased cost.

OBJECTIVES OF MOORLAND MANAGEMENT

These objectives are:

(i) To prevent re-colonization of heathland by shrubs and trees.

(ii) To prevent the development of stands of mature or degenerate heather, which would have a large biomass of wood and a high sugar content.

(iii) To provide uniform areas in which heather is regenerating, providing a high productivity of young edible shoots.

(Gimingham 1975)

Achieving these objectives provides a good habitat for Grouse and sheep, (with high capital returns), whilst decreasing the risk of large scale natural fires, most common and destructive in late mature and degenerate heather stands. All of these objectives are completely
fulfilled by burning but cropping only does so in part and the problems related to cropping are discussed later.

1.1.1. EFFECTS OF MOORLAND MANAGEMENT: PHYSICAL EFFECTS.

Although moorland management achieves the objectives required for good Grouse and Sheep conditions, its effect on other forms of management and use of moorlands can be quite profound; and of prime concern is its effect on water quality. Burning and to a lesser extent, cropping, affects the soil and consequently, water quality. The effects discussed in this section are primarily physical, chemical and biological but there are also secondary effects, both economic and ecological which are discussed in Section 4.1.0. The results of good and bad management practices and of natural fires are also discussed. Good management is becoming more difficult to achieve whilst the risk of natural fires is rising due to an increase in the number of drought years and greater public access. These risks are of course compounded by poor or inadequate management.

TEMPERATURE AND 'FIRE CHARACTERISTICS'

An understanding of fire characteristics, especially temperature, is essential in understanding the impact of fire upon heathland as they affect all the other changes directly or indirectly.
There have been many studies into the temperatures reached during heath fires which have produced differing results, Whittaker (1961), Kenworthy (1963), Kayll (1966). Recently, more detailed studies have been carried out in which variables such as fuel energy, fire intensity and rate of spread as well as temperature, have been considered, Hobbs and Gimingham (1984). These later studies of 'fire characteristics' have highlighted the reasons for disparities in the results of previous works, Gimingham (1975).

It is agreed that there is a general increase in temperatures of fires with increasing age of vegetation. Whittaker (1961), recorded temperatures at ground level mostly between 300°C and 500°C, with a maximum temperature of 840°C and suggested that temperatures were maintained for less than 2.5 minutes. Kenworthy (1963), recorded maxima of 500°C for ten years old heather, 700°C for 20 years old and 940°C for 35 years old heather, temperatures being maintained for less than 1.5 minutes.

Hobbs and Gimingham (1984) recorded fire temperatures in different Calluna phases, pioneer, building, mature and degenerate. Temperatures ranged from 340°C to 790°C in the canopy, and 140°C to 840°C at ground level and although large differences were occasionally found between canopy and ground level, they were generally found to be similar. Temperatures 1 cm. beneath the soil surface remained below
100°C and were maintained for up to 1.5 minutes, but for canopy temperatures above 400°C, temperatures at 1 cm beneath the surface were only maintained for a proportion of this time. This suggested that very little of the heat generated in the canopy was transmitted into the soil. Temperatures in degenerate heather were sometimes found to be lower than in mature heather, a factor found to be related to stand structure. Packman (1971) and DeBano, Dunn and Conrad (1977), suggested similar results, only 8% of the heat released by a fire being conducted into the soil.

For temperatures in the surface soil to rise above 100°C, all of the moisture must be removed, Cromer and Vines (1966), Roberts (1965). This is likely to occur only when heating is maintained for long periods as when 'natural' fires occur in drought years, where surface litter is removed and the soil ignited. Surface temperatures are related to ground layer vegetation and their varying moisture contents, heat yield declining with increasing moisture content (Byram, 1973). Mat mosses are found to be important in protecting surface soil as material with a moisture content of 300% or more of dry weight will not ignite. Temperatures at and below the soil surface therefore vary with the type of ground cover present.

Other 'fire characteristics' investigated by Hobbs and Gimingham (1984), include the intensity, width and severity of fires and weather variables. Fire intensity showed the same pattern as temperature, increasing with stand age up
to late mature and degenerate phases, when it declines. This is explained by differences in available fuel and the rate of spread of the fire. Rate of spread has the greatest effect, collapse of the *Calluna* canopy in degenerate phases alters the fuel configuration causing the fire to spread more slowly (Kenworthy, 1963). Rate of spread was twice as rapid in building phases than in pioneer and degenerate phases, indicating the importance of fuel disposition.

Age and height of *Calluna* have been related to changes in biomass and fuel distribution and it has subsequently been suggested that vegetation height influences fire severity, (Fritsh, 1927). Consequently, the Muirburn Working Party (1977) proposed that *Calluna* should be burnt before it reaches 30cm. tall. Fire severity was also found to be positively correlated with fire width, a factor which has important management implications.

Weather variables are considered to be of secondary importance, as long as they remain within 'normal' limits. Of primary importance is vegetation structure and amount and distribution of fuel. Hobbs (1981) found few significant correlations between fire and weather variables. Wind speed may affect the rate of spread but fuel disposition is more important. As long as the vegetation is dry enough to ignite, vegetation moisture content seems to be of secondary importance.
HYDROLOGICAL EFFECTS

Burning and to a small extent cropping, affect the hydrology of peat, especially in the surface layers where the effects are important as it is here where decomposition occurs, the relevance of this is discussed in Section 1.1.3. Hydrology is affected both physically, chemically and to some extent biologically, only physical effects are dealt with here.

Many studies have been conducted on the hydrological effects of burning and have produced conflicting results; posing the question, 'Do moorland soils become wetter or drier after burning?' Auten (1933) reported an increase in soil water infiltration capacity after burning in forests and fields in Ohio, Indiana, Michigan and Illinois, USA; Wahlenberg, Green and Reed (1939) found similar results. Imeson (1971), suggested that burning increased the volume and intensity of throughflow, leading to wetter hydrological characteristics on burnt land. However other researchers have reported a reduction in infiltration capacity. Rave (1971) working on burned plots of woodland chaparral in Sierra Nevada, reported a reduction of 90-95%. Kinako (1975) studying heathland soils, found infiltration on burned plots to be 50% greater than on non-burned plots. While Vehmeyer and Johnson (1944) working in California and Burgy and Scott (1952) working in chaparral sites of South Western U.S.A., found no reduction in infiltration capacity.
between burned and non-burned grazed areas. Mallik (1982) and Mallik, Gimingham, and Rahman (1984) found infiltration capacity to have been reduced by up to 75% on burned plots of heathland.

Mallik, Gimingham and Rahman (1984) largely answered these conflicting reports and thus their paper is discussed more fully. Their work was carried out in the South-West corner of the Muir of Dinnet National Nature Reserve, NE Scotland. In order to compare soil moisture conditions, two 10 x 20m. plots were marked out in late 'building' phase Calluna one of which was burnt (March 1979), the highest temperature recorded on the ground surface was 755°C and 767°C in the canopy. Specific interest was paid to the effect of burning on water infiltration, moisture retention, and pore size.

Results indicated that there was a highly significant difference in infiltration rates from the burned and non-burned plots. Burning was found to reduce infiltration in all cases, reductions ranging from 29% to 74%. Moisture retention curves indicated that the soil of the burned plot retained more water than the non-burned plot. These effects were greatest in the top 2cm of the soil and decreased down the profile. The top 2cm of the burned profile retained the highest amount of water at lower tensions and had the larger available water capacity. Mean pore diameter in the burned plot was found to be
1.0 \mu m. whereas in the non-burned plot it was 7.2 \mu m., these differences became less evident further down the profile between 2 and 6 cm. deep.

The substantial decrease in water infiltration on the burned plot was found to be in agreement with other authors (Heyward and Barnett, 1934; Heyward, 1936; Suman and Halls, 1955; Hanks and Anderson, 1957; McMurphy and Anderson, 1965). This is explained by the fact that the density of larger pores is reduced, with a subsequent increase in the density of smaller pores because ash particles on the burned plot clog the soil pores in the upper layers of the soil. The results for moisture retention and pore size support this theory. Pore size is also perceived to decrease in the surface layers on the burnt plot because much of the litter is destroyed during the burn (especially if high temperatures are generated). This replaces the uncompressed litter which has relatively large pores, by a compressed, partially humified layer with relatively small pores, at the surface. Changes below 2cm. are presumably less evident because ash particles have not descended to this level.

Conflicting results reached by other researchers were also discussed by Mallik, Gimingham and Rahman (1984). Veihmeryer and Johnston (1944) and Burgey and Scott (1952) were studying ecosystems markedly different from heathlands. In the case of Kinako (1975), A Heathland
Study, it is possible that his method of measuring infiltration capacity was unsatisfactory as Mallik et al (1984) found the method to be unsuccessful. Imeson (1971) does not report on how conclusions about infiltration or throughflow were arrived at, so it is difficult to comment on these conflicting results; his work was carried out over the winter period however, when the effects of burning, on soil moisture deficit, were likely to be at a minimum.

Drier hydrological conditions are also reported (small data set only) by Anderson (1980) in the Peak District Accidental Moorland Fires Report. Surface layers are most affected and the decreased moisture content of burnt areas still remains after three years. Differences between burnt and unburnt plots are greater on pure Calluna than on mixed or Eriphorum moor.

Crust formation can also lead to drier conditions in the surface layers of burnt peats. Three basic types of crust have been identified, (i) carbon or cokey crusts, (ii) thin skin-like crusts, and (iii) tough, fibrous, mat like crust, (Bridges, 1986). Although different types exist they usually form a heterogeneous coverage over a burnt area, depending on fire characteristics. High temperature fires, both accidental and managed burns, in old heather stands, form the most dramatic crusts.
Type (i) crusts occur on peat less than 100cm. thick, which is well humified and relatively dry which coincides with deeply cracked peat, indicating drying out and shrinkage of surface peat, to a depth of 10-20 cm., either before or soon after a fire. Type (ii) is a less extreme form of type (i). Beneath the crust is a layer of charred fragments. The surface is broken up by a dense network of shallow cracks, about 1cm. deep, indicating shrinkage of the surface layer, but not the underlying peat. Type (iii) is a very tough fibrous crust, widespread on poorly humified fibrous *Eriophorum* peat. The crust is uncracked and can be lifted off the underlying peat as a thick mat, smooth on the upper surface and very fibrous underneath.

Important questions have been raised about crust formation, it is unclear exactly when and how they are formed, and whether they result directly or indirectly from fires. Many authors have commented on the crustal features, for example Conway and Miller (1960) describe the result of severe burning on a loose textured surface peat where the surface becomes virtually amorphous, with a dense, cheesy texture, highly resistant to the passage of water through it, such a surface resembles the type (iii) crust. Several hypotheses have been proposed, it is likely that crusts are formed by a combination of factors which in turn depend on the fire characteristics, notably temperature. Suggestions for physical factors are:- (i) that crusts are formed by deposits of ash or charred debris produced in the fire;
(ii) that they are formed by intense drying out of the surface and (iii) that they result from weathering and drying out of the surface after the fire. Maltby (1990), describes granulation where by wetting and drying, heating and cooling and freeze thaw cycles all play a part in the process. Granulation and the subsequent erosion of hard crusts of charred peat can expose the underlying peat. This then dries out at the sub surface and develops a desiccation crust which contracts away from the deeper peat breaking the hydraulic continuity and is resistant to rewetting. This layer is then broken down into granules in its turn. The absence of vegetation cover in burnt areas can cause this process to continue progressively until vegetation is restored or the entire organic layer is lost. These factors have chemical implications and biological factors are also thought to affect crust formation; both these possibilities are discussed later.

Whatever their precise formation it is clear that crusts reduce the infiltration capacity of surface layers. Drying out of surface layers is a common factor, much lower moisture contents being found in surface crusts/layers than in underlying layers (Bridges, 1986). Moisture differences are most extreme in cracked surfaces, crust types (i) and (ii), which are produced in high temperature burns; differences in pH are also apparent, these crusts have values higher pH than layers below the surface, for example, crustal pH's 3.44 and 3.43 compared with 3.38 and 3.36 at
5cm. depth (Bridges, 1986). Crust type (iii), formed by moderate temperatures, also exhibits drier surface layers but to a lesser extent, the subsequent pH response is also less dramatic. Drying out is attributed to microclimate changes, rather than the direct effects of fire heating, biological processes also play an important role.

Crusts affect water relations dramatically, all three types reduce infiltration capacity but in types (i) and (ii) this may be overcome by water flowing between the cracks. However, this is likely to be negated by the chemical effects of water repellency.

Hydrology could also be affected in certain areas by cutting or cropping of heather as heavy machinery would almost certainly cause compaction in its tracks, thereby reducing infiltration capacity. However, this effect would be negligible compared with burning, as only a small proportion of the cropped area would be affected.

MICROCLIMATE
Numerous people have commented on the effect of burning on microclimate and most agree that burning leads to an increase in evaporation with a subsequent decrease in soil moisture, especially at the surface. Burning causes change in all the parameters that govern microclimate; humidity, surface temperature, evapotranspiration, wind speed and irradiance. Whittaker and Gimingham (1962) recorded
increases in daily and seasonal temperature fluctuations. More rapid heating was caused by the increased albedo arising from blackened soil; followed by cooling. Humidity was reduced owing to increased evaporation from bare ground. Gimingham (1972) also showed that hill heather canopies reduced the surface wind speed and hence, evaporation, especially in building and mature stands. Temperature differences of 5 to 10°C were found between canopy and ground levels on sunny days, illustrating the insulating affect of heather cover. Mallik, Gimingham and Rahman (1984) also suggest that differences in evapotranspiration rates affect infiltration into the soil. Bridges (1986) suggested that differences in microclimate may also enhance crust formation. This conflicts with Imeson (1971) who states that eliminating interception and transpiration, increases the volume and intensity of throughflow, which suggests that evapotranspiration is greater than evaporation from a bare surface.

Studies comparing potential water loss from Pteridium in its natural state with that from litter covered ground (a herbicide having been applied) also show evaporation from the litter site to be greater than evaporation and evapotranspiration from the natural site (Martin, 1985).

The effect on microclimate is diurnal; bright, sunny, and windy days causing the greatest differences in water loss from both burnt and unburnt sites. At night rapid cooling
of bare surfaces can cause frost heave which accelerates erosion, especially when this is coupled with increased wind speed.

The cropping of heather moorland must also alter the microclimate and affect parameters in a similar way to that of burning. The overall effect is likely however to be less dramatic as infiltration is only affected where compaction occurs and there is no increase in albedo due to burning.

**EROSION**

Burning is generally accepted to increase erosion as it exposes the surface of the peat and removes vegetation which would otherwise produce litter. The severity of erosion is not constant however as it is dependent on several factors such as climate (macro and micro), grazing pressure and severity of burn. Slope is generally not important as the range of moorland gradients where heather grows is usually low (Imeson, 1971).

Macro-climates of moorland areas provide the necessary conditions to remove particles of peat; high and often intensive rainfall, low temperatures and high wind speeds; these conditions are enhanced by changes in microclimate. Burnt surfaces are more exposed to rain splash and runoff; high surface temperatures during the summer accelerate drying and low surface temperatures in winter cause frost
heave, loosening particles which are removed by higher wind speeds or increased runoff. Arnett (1980), noted that lack of protection from rain drop impact and surface wash, due to the absence of vegetation, could accelerate erosion rates by a factor of 20. Winter rates of erosion were found by Imeson (1971) to be ten times higher, due to increased runoff and needle-ice development, on bare ground where the peat had been exposed. However, where ground was insulated by litter or vegetation, summer and winter erosion rates were not found to be significantly different.

The severity of burn can also affect the degree by which erosion is increased; infiltration capacity decreases whilst water repellency increases, leading to an increase in surface run off and overland flow, promoting erosion, especially when burns are large and uncontrolled, Kinako and Gimingham (1980). The temperature of the burn also reduces soil moisture and produces peat aggregates for erosion. Imeson (1971), found that in dry windy weather there was an almost continual removal of plant remains and peat aggregates from burnt ground. Later discussion shows that fire severity also affects the rate of revegetation. As fire temperature increases, the length of time required for revegetation also increases and the amount of time during which the surface is exposed thereby increases. Depending on fire characteristics, throughflow and infiltration capacity may be increased on bare ground,
during winter months, due to lack of interception and evapotranspiration, which enhances erosion.

Grazing pressures also increase erosion. As sheep congregate in bare areas, where movement is easier, they loosen the peat surface, Grant et al (1982), and where grass is not available they eat young heather shoots, which slows down the process of revegetation (as discussed later).

The scale of the above factors affect the amount of erosion, fire characteristics being of primary importance, even, 'normal', well managed burns cause erosion. Imeson 1971 stated that: - (i) Erosion on bare ground; surface of peaty or mineral subsoil equalled - 45.3 mm/year and (ii) Erosion on bare ground; surface of burnt Calluna and raw humus equalled 9.5mm/year.

Even after revegetation had begun, erosion was still present until complete canopy cover had been reached, vegetation height and cover were found to be related to erosion. Rates recorded for Calluna of varying heights were as follows:-

(i) 5 - 15 cm high; 10 - 100% cover, - 6.4 mm/year,
(ii) 15 - 20 cm high; 40 - 100% cover, - 0.74 mm/year,
(iii) 20 - 30 cm high; complete canopy, +0.25 mm/year,
(iv) 30 - 40 cm high; complete canopy, +3.81 mm/year.
Such erosion leads to an increase in runnels, development or extension of seepage faces and removal of material lower in the soil profile, promoting development of gullies. These features occurring on, or down slope of, recently burnt ground. Erosion in this case is essentially short term (2 - 4 years) and continues at an accelerated rate only as long as it takes *Calluna* to restore complete canopy cover. Severe fires (usually accidental) can however cause dramatic effects, leading to the formation of peat 'hags' separated by gullies, down to the underlying mineral material, Gimingham (1975). In such cases the topography of the moor may be dramatically altered and stabilization may take many years. The surface peat can even be largely removed in extreme cases, carbonized by intense burning. Some moors may never recover, for example Glaisdale Moor suffered a severe fire in 1976, parts of it were carbonized and still exhibit large areas of bare peat 14 years later, Bridges (1986).

Cropping is also likely to increase erosion, but only to a small degree and for a short period of time. Wind speeds and rain splash will increase, due to removal of the vegetation canopy, but the surface remains protected by surface vegetation such as mosses, grasses and *Eriophorum*, bound together by heather roots (which may not be the case in instances of severe fire) and insulated by a litter layer. These low rates of erosion will however, only last as long as it takes canopy cover to be regained. Erosion
rates are likely to be highest in areas of monoculture Calluna where surface protection is at a minimum.

NUTRIENT STATUS

The nutrient status of moorland is affected by direct and indirect burning to a degree related to the pre-burn vegetation characteristics which generate subsequent fire characteristics. Direct effects cause plant nutrients in the vegetation canopy to be mobilized in the form of ash or smoke. Indirect effects include leaching and removal through surface wash, of nutrients from the ash, litter and soil and in extreme cases, erosion may cause large scale loss of nutrients. However, the input of nutrients is ongoing, which may reduce or restore any losses from the nutrient cycle.

Direct losses have been widely studied, based primarily on losses of Calluna on ignition as it usually represents over 90% of the dry matter present; nutrient composition of other species is generally similar. The elements which suffer greatest losses are those which form volatile compounds - carbon, nitrogen and sulphur. Kenworthy (1964) demonstrated that as temperature increased so did the quantities of nitrogen released from Calluna, amounts rising steeply above 300°C and continuing to about 80% loss at 800°C. Other losses included potassium and iron, significant above 400°C and phosphorous, significant above 600°C. Nitrogen released was found to increase with fire
duration at high temperatures and this may also be true of other elements. Experimental losses are however, likely to be higher than the actual losses because ignition lasted five minutes whereas managed heath fires rarely last as long. However, it indicates the potential losses in cases of mismanaged or accidental fire. These results were closely paralleled by Allen (1964) and Evans and Allen (1971).

Not all these nutrients contained in the smoke from a heath fire are necessarily lost, some may be deposited or condense nearby, Allen (1964). Evans and Allen (1971) found that only a very small proportion was deposited within a distance of 120m, commenting that convection currents could carry particles high into the air stream removing them from the heathland. Losses must occur and increase with increasing fire temperature, so that if the temperature can be prevented from rising above 400°C the losses of important nutrients, apart from nitrogen, can be minimized. This provides another reason for carefully controlling the intensity and temperatures of heath fires.

Indirect effects on nutrient balance have two main aspects; what happens to the ash and the nutrients it contains and what is the effect of the fire on potential nutrient inputs?
Ash and the nutrients it contains, are affected by soil type and the temperature of the burn. Allen (1964) demonstrated that peat and clay soils retained important quantities of nutrients, especially K and Ca, from solutions similar to those passing through the soil during the natural leaching of heather ash. These soils contain the greatest amounts of colloidal material, which controls the adsorption capacity and infiltration rate. Ash particles also reduce infiltration by clogging the pores in the surface layers. However, sandstone soils lost K when treated with leachate and gained little Ca, Mg, or P. Natural leaching following burning could clearly lead to loss of nutrients, due to the greater hydraulic conductivity of sandstone soils.

*Sphagnum* found on peat soils also exhibits strong absorption properties for nutrients, described by Clymo (1963) and others. On wetter heather moors *Sphagnum* reduces losses through surface drainage, and readily adsorbs K, Ca, and Mg ions.

Temperature of burning is important as it affects the infiltration capacity of the soil, thus affecting its capacity for incorporating ash. Following normal temperature burns, the surface is largely unaffected and ash is washed into the soil, where it then reduces the infiltration capacity and reduces the effects of leaching. High temperature burns may however cause crusts to form chemically, much reducing infiltration and exposing the ash
to surface wash, resulting in removal of nutrients from the site.

Potential nutrient inputs are also largely affected by fire temperature. In well managed burns, losses during a fire are readily replaced by the input of nutrients in the interval between fires, Chapman (1967). Accidental or poorly managed fires present a different case however. Loss of nutrients is high due to high temperatures and the litter layer is often removed which means that there are no inputs from humification, regeneration is severely retarded and less litter is produced for subsequent decay. In such cases, loss of nutrients is likely to be severe, leading to an impoverished moorland, susceptible to erosion.

Other important nutrient inputs include those from rainfall, grazing animals, and microbes. Rainfall provides ample sulphur to make good any losses and replaces Ca and Mg easily, Allen (1964), similar conclusions were reached by Robertson and Davies (personal communication to Allen) (1964). Losses of nitrogen and phosphorous can only be replaced by rainfall if the vegetation and soil retain almost their entire income of nutrients over a number of years, Allen (1964). As revegetation progresses, the speed of replacement increases. Fowells and Stephenson (1934) and Tamm (1950) considered that increased activity by micro-organisms, after burning, could make good the losses of available nitrogen, presumably by mobilizing part
of the fixed soil nitrogen rather than by fixing new N from the air.

Whilst it was previously thought that burning was harmful to soil fertility, these studies indicate that well managed burning does not have any serious effect. However, poorly managed or accidental fires can have a devastating effect and cause absolute losses which are difficult to replace from inputs; unlike well managed burns where equilibrium is readily restored. Once the circulation of nutrients has been disrupted a serious depletion occurs as shown by experiments at Hubbard Brook (Borman and Likens, 1970; Borman et al, 1968; Likens et al, 1970). In these experiments the use of herbicide prevented new growth and there was no take up of nutrients released by decaying vegetation. Severe burning would have a similar detrimental effect.

Therefore, not only the direct physical and chemical affects of burning must be considered but also the associated indirect factors such as erosion, grazing and damage to the peat through burning and drying out of the denuded surface.

The effect of cropping on nutrient status is dependent on the precise method used. Whilst methods of actual cropping do not differ, methods of dealing with the products can do so because litter is either finely cut and is widely
dispersed, or it is raked up and burned. Cutting and dispersal does not represent a direct loss but it may cause losses by wind dispersion and leaching, but these are likely to be much less pronounced than on a burned site. Nutrients will however, take much longer to be released from the litter as it has to decay, in contrast to burning, where ash is already in a useable form. Regeneration may consequently be slowed down as there is no immediate input of useable nutrients to replenish an already nutrient poor soil. Raking up and burning of the cut litter may also represent a loss, depending on the efficiency of raking up, the severity of burning and the destination of the resulting ash. In addition raking may disrupt or remove the litter mat from the top of the soil surface, leading to possible surface wash, erosion and the removal of a valuable nutrient source. These potential losses can only be replaced by spreading the ash resulting from burning the cut litter, back over the area that has been cropped. It is unclear whether this practice occurs.

1.1.2. CHEMICAL EFFECTS

THE EFFECT OF DRYING ON THE COLLOIDAL PROPERTIES AND STABILITY OF HUMIC COMPOUNDS

As discussed in previous sections moorland burning can cause drying out of surface peats, drying can be direct in severe fires, but more usually is indirectly caused by
changes in peat hydrology. Such changes affect the organic matter content of peats.

Organic matter in peats is largely composed of humic compounds, which are characterized by their stability and resistance to chemical and microbial decomposition. Environmental factors which lead to drying and wetting cycles or freezing and thawing cycles are known to decrease the stability of organic matter, (Raven and Arnimelech, 1978). These conditions can result from moorland burning, their severity depending on fire characteristics.

The effect of drying on the stability of the organic matter in soils has been attributed to partial sterilization and to changes in the colloidal properties of the organic matter, Birch, 1958a. However, partial sterilization has been shown not to be the major factor by a number of researchers, including, Birch 1959, who has shown that the effect of drying is at least partially due to changes in the organic colloids. Comber (1922) assumed that the decrease in stability was caused by the fragmentation of the organic gel by drying, leading to the exposure of a greater surface area.

Raven and Arnimelech (1978) demonstrated that drying of soil is accompanied by the destruction of bonds, presumably hydrogen bonds, between organic polymers. This process is correlated with the exposure of fresh surfaces and a
subsequent high rate of organic matter decomposition. It is shown that drying causes the availability of organic matter to micro-organisms to increase, this is discussed further in the biological section. Drying also has a marked effect on the solubility and dispersability of organic matter in the soil. Organic macromolecules in the soil are aggregated due to hydrogen bonds formed in the presence of water. When soil is dried this structure breaks down and the stability of the organic matter decreases. In a wet soil a substantial number of the organic molecules are prevented from contacting the soil solution in the aggregated structure, this is indicated by the lower acidity in the wet soil and accounts for one of the important factors contributing to the stability of humic compounds. Instability caused by drying leads to an increase in soluble organic matter (extracted with water) and in the dispersion of organic matter (extracted with 1N $\text{Na}_2\text{SO}_4$). The potential for denitrification (discussed later) and acidity also increases.

Acidity is thought to increase owing to either hydrolysis or oxidation of organic compounds, or the increase in the exposed surface area of peat aggregates and their associated acid groups. Chemical hydrolysis and oxidation is not thought to be a reasonable explanation when peat drying is considered, especially if the time involved is short. The process of destabilisation is not instantaneous and apparently requires some relaxation period for complete
dispersion of the organic matrix, however, changes are most prominent in the first stages of drying and they level off gradually. In particular, hydrolysis is unlikely except in high soil temperatures conditions - above 100°C, usually only found in severe fires, as discussed in Section 1.1.1. Partial oxidation of organic matter may occur in newly exposed surfaces if prolonged drying takes place. Structural changes are thus considered to be the most plausible explanation when peat drying is involved. Humic compounds are known to exist in complex geometrical structures which are stabilised by water molecules, once these are removed a slow process of decoiling takes place exposing sites for microbial attack.

THE EFFECT OF FIRE ON SOIL HUMIC SUBSTANCES

Moorland fires initiate many indirect effects on soil humic substances, usually involving some element of peat hydrology. However, in cases of severe fires, usually following a drought, direct effects on humic substances may be produced but these are probably limited to accidental fires.

Direct effects of temperature on humus have been studied mainly in the laboratory, using such techniques as differential thermal analysis (DTA), differential thermal gravimetry (DTG), thermo-gravimetry, isothermal heating and pyrolysis. Following such work Orioli and Curvetto (1978) suggest that only temperatures over 250°C. produce changes
in humic fractions. Hence, changes are likely to occur in accidental fires, where the surface peat ignites and smoulders, due to the high temperatures reached. In normal managed burns soil temperatures do not usually exceed 100°C. at 1cm depth, declining to just a few degrees centigrade increase at 5 - 10 cm depth, because of the high water content of peat soils.

Results show that below 300°C., humic acids are mainly composed of grey and brown colour bands of high molecular weight and low mobility, although some yellow colour bands of low molecular weight and high mobility are present. Above 300°C., the grey and brown colour bands gradually disappear due to decarboxylation and oxidation of the humic molecule, changes occurring in the core separation patterns of the different subfractions. This leaves only the yellow bands, above 400°C., which are soluble in aqueous alkali solutions. The nucleolus of these yellow substances has a net negative charge, possibly due to carboxyl and hydroxyl groups still being present. At temperatures of between 500°C. and 600°C. the yellow colour bands also disappear, no alkaline soluble coloured substances remaining. This shows that soils lose an appreciable amount of organic matter when temperatures rise above 300°C. and indicates that all humus may be volatilized above 500°C.

Normal burns, observed by Orioli and Curvetto (1978), show no direct changes to soil humus after burning since soil
temperatures are low. They comment however that: "the presence, after burning of partially burnt organic residues, generally results in a more rapid mineralization and mobilization of soil nutrients stored in the superficial raw humus layer", suggesting it is possible that normal burning has an indirect and more gradual effect on the physical and chemical properties of soil humic substances.

FIRE INDUCED WATER REPELLENCY

Water repellency can occur directly, as a result of fire, or indirectly, due to biological factors (discussed later in the biological section). Many researchers have been involved in assessing the mechanism involved in fire induced water repellency. DeBano and Krammes (1966) showed that wildfires on certain watersheds caused extreme water repellency, creating excessive runoff and resulting in serious erosion and delays in revegetation (Krammes and Osborn, 1968). Debano and Krammes (1966) proposed that this phenomenon was due to the vaporization by the fire of hydrophobic substances at the soil surface which then migrate down the soil profile and condense in the cooler areas. Cony and Morris (1968) suggested that hydrophobic substances melted and migrated down the profile possibly forming organo-silicate complexes between the translocated substances and soil particles.
DeBano (1966) demonstrated in laboratory studies, that plant litter heated over a wettable sand, caused water repellency in the sand. The water repellent layer was formed below and parallel to the soil surface, the ash-dust and surface layer remaining wettable. The thickness of the layer and its degree of repellency was found to vary, depending on the temperatures involved and their duration. The temperatures used ranged between 148°C. and 482°C. for durations of 5, 10, 15, and 20 minutes. Heating at 148°C. for all durations did not appreciably increase water repellency, whereas heating at 204°C. for 15-20 minutes did so. Water repellency was destroyed at higher temperatures, at 426°C. it began to decrease and at 482°C. the soil became completely wettable, presumably because all the organic matter had been volatilized.

Savage, Martin and Letey (1969) proposed that the substances condensing in cooler portions of the soil were actually pyrolytic products of the heated litter layer rather than organic materials translocated after a simple volatilization. Aliphatic hydrocarbons and related substances, which were characteristic of pyrolytic reactions, were captured moving from a heated soil and shown to be capable of causing water repellency in treated sand (Savage et al, 1972). Soil litter and possibly its cellulose constituent in the litter were shown to be the source of these substances. It was postulated that a natural fractionation of the substances occurred as they
moved into the soil, with the more polar materials condensing higher in the soil profile. The theory was also proposed that these condensed substances were fixed by the heat passing down the soil profile from the surface fire.

Further work by Savage (1974) supported these theories and following his own work and that of other researchers mentioned, he suggested the following mechanism by which extreme water repellency is induced in burned-over soils.

(i) The fire passes over the soil surface, hydrophobic and hydrophillic substances are produced from organic litter.

(ii) Some of these substances move to the underlying, cooler part of the soil and condense. The depth of the condensation area is probably quite narrow and because of the presence of hydrophobic and hydrophillic substances, the water repellency induced is not extreme. The actual quantity of organic material produced from the litter and the relative amounts of hydrophobic and hydrophillic substances present, probably depend on the intensity and duration of the fire and the quantity and moisture status of the litter.
(iii) After passage of the fire, heat from the surface moves down the soil profile over the condensed organic substances. Temperatures exceeding 250°C. 'fix' the more polar hydrophobic substances in place. The remaining 'unfixed' substances are revolatilized and migrate deeper into the soil before recondensing.

Surface litter is thought to be the main source of volatile substances such as waxes, resins and oils, since the heat of volatilization is usually only reached at the surface. The penetration of heat is very limited in peats due their high moisture contents.

Induced water repellency is possible in all burnt-over soils and as such may play a part in crust formation. The degree and depth of induced water repellency varies with fire intensity, severity, subsurface temperatures reached and the amount of litter present. Normal managed burns are likely therefore to impart only a slight increase in repellency, the products of which are subject to extraction. Alternatively severe fires, especially after drought, are likely to produce extreme water repellency in soils, the products of which are difficult to extract, and lie in a wide layer. Maltby (1990), describes water relations in altered surfaces at Glaisdale following the chemical effects of burning, describing them as unable to retain or absorb moisture.
1.1.3. BIOLOGICAL EFFECTS

REGENERATION AND GERMINATION

These subjects are mentioned briefly because although they do not affect colour generation directly, they do affect the length of time during which other processes influence peat hydrology and therefore colour production.

Heather regenerates both by vegetative growth and by developing new plants from seeds. Vegetative regeneration involves the production of clusters of young shoots from old stem-bases, which usually survive the passage of fire. Normal management burns clear away all of the plant above the stem bases, buried either in the soil surface or in the surface litter, mosses and lichens. On these stem bases lie the reserve buds, protected by the litter layer from all but major rises in temperature. These buds produce young shoots which develop rapidly as they are able to draw on the fully developed root system of the former plant.

Germination of seedlings relies on suitable conditions, and often supports vegetative regeneration. Where vegetative regeneration is not possible, seedlings present an alternative, but regeneration is comparatively slow. Up to six years may elapse before full cover is attained compared with the two or three years during which vegetative regeneration occurs. Seed germination and seedling development is especially suited to peat moorland
where the surface is largely organic matter, which has the ability to retain a high degree of soil moisture. Management by burning also stimulates germination by allowing more light to reach the seed bank and by giving rise to fluctuating temperatures which occur because bare peat has a low albedo, causing the surface to warm rapidly during the day and cool rapidly at night, Gimingham (1972). Fire itself may also act as a stimulant to germination for experiments have shown that the number of seeds germinating and their rate of germination, is increased by short periods of heat treatment, (Gimingham, 1972) at temperatures ranging for example from 160°C for 25 seconds to 40 - 80°C for one minute. Such temperatures are reached just below the litter surface in normal management burns which normally leave a more compact seed-bed than is provided by loose, fresh litter (Gimingham, 1975).

Heather may be regarded as a fire adapted species due to its ability to regenerate by such methods. Regeneration does not however follow a simple pattern as there is considerable variation in post fire vegetation response. Whittaker (1960) and Gimingham (1972), suggested that both stand characteristics and fire severity were important determinants in the post fire response or revegetation. Stand characteristics are important in relation to the growing phase of Calluna, it is known to decline in its ability to regenerate vegetatively as it grows older (Mohamed and Gimingham 1970). The building phase has the
greatest number of nodes at the base of the stem, these decline in the mature phase, and become rare or non viable in the degenerate phase as the heather plants thin out. The seed bank below *Calluna* is usually supported by large numbers of seeds which retain their viability for several years. Fire severity is also important since surface temperatures above 400°C are lethal to stem bases, which could destroy a large proportion of the potential for vegetative regeneration. Seed banks are also at risk in severe fires if the surface litter becomes ignited. Hobbs and Gimingham (1984), have shown that fire severity is mainly a function of stand structure and therefore, the two are not independent.

Hobbs (1981) found no clear relationship existing between fire severity and the ability to regenerate following normal management burns, concluding that the effects of fire severity were of secondary importance to those of pre-burn characteristics. Such findings are liable to hold true since temperature generated in normal burns is not sufficient to damage stem bases or seed banks.

These findings highlight the importance of good heath management, for problems cannot be corrected by good fire management alone. Ideally, heath should be burned in the late building to mature phase which avoids revegetation problems. However, as previously discussed, longer intervals between burns allow heath to develop into late
mature and degenerate phases causing problems both in terms of the age of Calluna and in fire severity. As nodes have been destroyed, little vegetative regeneration occurs and recovery depends on the seed bank which will have been depleted owing to the high temperatures reached and little seed remains in the burned areas (Mallik, Hobbs and Legg, 1984). Recovery of the stand is considerably slower than that which follows burning of younger stands and bare ground may still persist for up to eight years after the fire (Hobbs and Gimingham, 1984). This bare ground may also be detrimental to Ericaceous seedling survival (Mallik and Gimingham, 1983). Severe fires also produce crusts, which affect seedling growth due their compact nature, low humidity and low soil moisture.

Secondary successions can also affect the surface and seedlings after burning, especially where burning is severe, as other species are removed and do not recolonize so quickly because they are not fire adapted. In such cases the bare ground is quickly recolonised by gelatinous green algae, lichens and mosses, their spread depending on the amount of moisture at the surface. Moisture on the surface is increased by reduced infiltration which follows severe fire, so the spread of these species can be rapid, especially in the absence of other competing species. This reduces the effect of fire on microclimate as the albedo of the surface is increased. The amount of water available to seeds and seedlings is further reduced where these species
colonize because they secrete substances which induce water repellency (discussed later). The floristic composition of the stand before burning also greatly affects secondary succession and determines which species recolonise and it subsequently affects the amount of Calluna. This is of little direct importance to colour generation as it is the protection of the peat which is important, not the species involved. They are however vitally important to gamekeepers and grouse rearing; for further details see Hobbs and Gimingham (1984). Effects of severe fire on vegetation recovery are also discussed by Bridges (1986), relating to Glaisdale on the North Yorkshire Moors where large expanses of bare peat still remain, fourteen years after the fire.

Cutting can provide an alternative to burning, but as with burning, regeneration is quickest when the plants are aged six to ten years, (i.e. building or early mature phase), after which regeneration declines to a minimum in the 26 to 30 years age class (late, mature or degenerate phase). Cutting may leave more nodes for regeneration than burning, as it only removes part of the branch system leaving a greater number of sprouting positions. Disadvantages do occur with this method however, branches lie where they fall interfering with regeneration, suppressing young shoots and seedlings or they are removed, depleting nutrient supplies. Seeds do not benefit from the passage of fire (discussed previously) and only a small proportion of heath is suitable for cutting.
Cutting does not provide an alternative to burning late mature or degenerate stands, where high temperatures are reached, since vegetative regeneration is extremely low at these ages. Regeneration is mostly from seed which does not receive benefits from the effects of cutting.

Clearly, poor heathland management caused mainly by under management since 1945, can lead to considerable problems as far as regeneration is concerned leaving large tracts of land bare for up to eight years and for much longer, in cases of extreme fires (usually accidental). This presents problems for gamekeepers and farmers but also has many ramifications as far as colour production is concerned; maintaining and exacerbating those changes in peat hydrology caused by burning, (previously discussed).

**SHEEP GRAZING**

The effects of sheep grazing on burnt moorland can be two-fold; too many sheep cause revegetation problems, no matter how well burns have been managed and even the correct grazing pressure can cause problems in severely burnt areas.

Grazing affects the succession of vegetation due to retardation, demonstrated at Bowhat, Arnfield, in the Peak District where moorland, burnt in 1959, had recovered its heather cover by 1967 where it had been lightly grazed but
was still bare where grazing was more intense, (Phillips, Yalden and Tallis, 1981), sheep congregate in bare areas where movement is easier (Grant et al., 1982). Where grass is not available they eat the young heather shoots, or plants; grazing of shoots renders them more susceptible to desiccation, particularly young plants. Grazing can also suppress flowering and thus the attendant production of seed, a factor of major significance in recolonising moorland, especially if severely burnt (Yalden, 1981), slowing down the cumulative spread of vegetation.

Over grazing also leads to accelerated erosion on burned moorland (Yalden, 1981). The effects of sheep-initiated erosion are likely to be exacerbated by the effect sheep themselves have on delaying vegetation colonisation and invasion. Lack of protection by vegetation leads to removal of peat particles by trampling sheep and leaves the bare ground open to erosion by raindrop impact and surface wash. These are factors that can accelerate erosion rates by a factor of 20 (Arnett, 1980). Such combined effects can result in severe problems for the long-term recovery of burned moorland.

A maximum grazing intensity of 2.4 ewes/ha (Grant, 1983), is recommended by the Hill Farming Research Organisation in order to prevent progressive decline in the area of Calluna on moorland with 100% vegetation cover. On wetter moorland, this should be reduced to 0.5 ewes/ha (Rawes
Where burning has reduced vegetation cover to less than 100%, these figures should be proportionally reduced. Sheep are likely to have the greatest effect during the recovery phase, on species composition and recovery time and therefore their numbers should be kept to a minimum during this period.

**BIOLOGICALLY INDUCED WATER REPELLENCY**

As previously mentioned both physical and chemical effects can lead to the drying out of surfaces and generally speaking the magnitude of the effect increases, with increasing temperature. This is also true of biological effects, but rather than being entirely linked to temperature, they are also indirectly governed by the rate of revegetation/regeneration.

Water repellency is caused by the spread of lichens, algae and fungi after fires and may explain the formation of some crusts, (Bond and Harris, 1964). Miller and Wilkinson (1977, 1978) demonstrated the association between fungal growths and water repellency, fungal mycelia coating soil particles and preventing rewetting. Gimingham (1970, 1972) and Hobbs and Gimingham (1984) suggested that lichens were responsible for the crusts commonly observed after heath fires. Bridges (1986), commented that lichen was a widespread colonist on Glaisdale Moor, Maltby and Legg (1981) commenting that growths of fungi, lichen and algae
contributed to gelatinous surfaces on samples of crust from Glaisdale.

In addition to post fire growths, there is considerable evidence that the products produced by lichens, algae and fungi are altered by heat. Savage et al, (1969) indicated that several common fungi produced materials which became strongly water repellent on heating. Savage (1972) found that soil litter was the main source of heat-induced water repellency and that fungi incorporated in the litter were the most likely manufacturers.

The degree to which lichens, algae and fungi colonise areas is governed by the rate of revegetation. Following well managed burns, regrowth can be so rapid as to establish nearly 100% cover before any colonization of the exposed raw humus or peat can occur. Generally patches do occur however, but the areas occupied by these species have been shown to reach a maximum in the first or second season after burning, (Gimingham, 1972). If revegetation is slow, for example due to over grazing or high temperatures, colonization of the surface may occur, which itself inhibits further revegetation, as induced water repellency creates a poor environment for the germination of heather seeds. These colonists also survive in a nutrient poor environment and can therefore readily colonise severely burnt moorland. Maltby (1990), describes a veneer of predominantly filamentous algae and moss which was
established in the first year after the fire. Gelatinous and coccoid algae partially colonising the charred peat in association with lichens. This surface film repelled water and was inhibitory to the germination of seeds. This succession was evident between 1976 and 1979.

Whittaker (1960) pointed out that the rate at which these secondary successions took place was determined by the rate of regeneration of Calluna and other Ericaceous species and this in turn was governed by the age of the stand before burning, the intensity of the fire and the environmental conditions during and after burning. Therefore management should be aimed at rapid regeneration, minimizing the succession stages described above.

EFFECTS ON MICROBIAL POPULATIONS AND C:N RATIOS

Burning initiates many interrelating effects, the consequences of which result in a drier hydrology in the surface layers of peat, the degree of drying being dependant on the temperature of the burn. Such changes in turn lead to greater microbial activity resulting in low C:N ratios.

Maltby (1980b) and Maltby and Edwards (1981) found a variation in the microbial response to different degrees of burning. Very high counts of aerobic microbes were obtained from certain peat surfaces which had undergone 'normal' burns. These were two orders of magnitude greater
than the numbers in unburnt peat and also greater than numbers in severely burnt peat. This implies that oxidation of peat can be greatly aided by controlled burning.

Maltby (1980a) NYM, used C:N ratios to assess microbial activity in peats under different management/burn conditions. Carbon is lost where biological activity is greatest but nitrogen is retained, resulting in low C:N ratios. Maltby's analysis of peat profiles on both fire-damaged and normally managed areas of Rosedale, North Yorkshire Moors, revealed an unusual pattern of C:N ratios. The trend of steadily declining C:N values was reversed at 5-8cm. depth, suggesting strong humifying conditions immediately below the surface peat. Exceptionally large numbers of bacteria were found in those peats which were burnt in the uncontrolled summer fires of 1976 at an intensity most closely approximating to conditions in a normal management burn. Oxidation effects were also associated with structural cracks in the peat, as low C:N ratios followed the line of the cracks, owing to increased microbiological activity. Such micro-organisms are involved in the process of decomposition of organic substances.

Maltby (1980) NYM also studied microbial numbers in peat profiles by the soil dilution plate method, estimating the numbers of fungi, yeasts, actinomycetes and bacteria. In areas where the fire had been intense and charred granular
peat had formed a crust, low numbers of micro-organisms were found; explained by the fact that such materials have an inability to retain water and a lack of easily available organic substances and nutrients. In other areas, where the fire had been less intense, an intact surface remained, able to retain moisture and to support very large numbers of micro-organisms, mainly bacteria. Such numbers were attributed to the sudden availability of organic substances in the form of severed roots and nutrient addition from ash. Thus low intensity, short duration burning, most closely related to 'normal' burning, seems to lead to the greatest increase in microbial numbers.

Coupled with the effect of increased microbial numbers is the increase in the number of rewetting cycles on burnt moorland (for physical and chemical reasons mentioned previously). Birch (1958a) has discussed this relationship at length, pointing out that increased numbers may well be in response to the increase in the number of rewetting cycles. Respiro-meter experiments show that when a dry soil is moistened, a characteristic pattern of decomposition occurs. After an initial period of relatively rapid decomposition, which slows down over a few days, it shows a steady rate followed by virtually no decomposition, when dry conditions are restored. This pattern is repeated with successive drying and rewetting.
The magnitude of decomposition depends on the percentage carbon in the soil and on the drying conditions, air drying being less effective than oven drying, an effect which is potentially mirrored by burning, surface temperatures generally reaching between 60°C. and 100°C. Curran and Evans (1947) postulate that following heat shock, spores are stimulated to intense metabolic activity which partly explains the marked decomposition that follows oven drying. Evidence shows that decomposition involves direct microbial attack on the solid organic substrate and that the recurrent pattern of decomposition is due to the state in which the microbial population is left after drying and its subsequent behaviour on rewetting, Birch (1958).

The decline following rewetting is not thought to be because of the development of toxins, physical changes in the soil, or in the depletion of organic material made soluble by drying, but rather due to the physiology of bacterial populations. Subsequent germination and multiplication after drying being comparable to the early phase of a bacterial culture, where metabolic activity is very much greater than that of later generations, developing after the period of maximum multiplication.

The initial rate of decomposition could be explained by this factor, activity declining as rewetting progresses, the culture passing into the resting stage.
Birch (1958a), addresses burning and states directly that any agricultural practise that enhances drying, leads to more nitrate production when rewetting occurs. An effect caused not by the small, direct, alteration of humus by burning but by the increased decomposition that follows, when burned soils are rewetted.

1.2. BACKGROUND, CURRENT PROPOSALS AND REVIEW OF THE LITERATURE (RELATED TO COLOUR), ON MOORLAND LIMING.

1.2.0 LIMING MANAGEMENT.

HISTORY AND REASONS FOR LIMING. Calcium and Magnesium are essential plant nutrients and as such it is necessary to replace those ions utilised by crops and/or lost from the soil by leaching. Lime applied to soils replaces these nutrients and also has the benefit of adjusting or maintaining soil pH to provide optimum growing conditions. Such practices improve acid soils and allow grassland swards to become high yielding pasture. Liming of extensive areas of grassland has become part of overall agricultural improvement in Britain, but its popularity has fluctuated over time, depending on the level of subsidies paid.

The use of lime declined during the second half of the 19th century; having become popular during the agricultural
revolution, usage increased in the late 1930s, following the introduction of the Land Fertility Scheme and Government subsidies to encourage the use of lime in agriculture. The amount of lime, applied to land, in the UK increased 3.8 fold during the years 1939 to 1943 and 1959 to 1963, (Agricultural Development Advisory Service, 1984), after which there was a marked decrease in its use. The greatest decline being caused by a change in the way the liming subsidy was calculated, from one based on percentage costs, to one based on fixed costs (Agricultural Lime Products Council and, the British Aggregate Construction Materials Industries, 1983).

Before 1964, lime subsidy was paid on the basis of 50% or greater, of the fixed cost. In 1964 the subsidy paid changed to one based on fixed scales of assistance on haulage and/or materials. Further, the subsidy fell from 50% of average cost to about 25%, as lime and haulage became progressively more expensive, the effects of haulage prices being dominant. It has been estimated that following these changes the usage fell in Wales by 56%, Northern Ireland (66%), England (48%) and Scotland by 35%, during the period 1959-1970 (Ministry of Agriculture Fisheries and Fisheries, 1959, 1966-70). Finally, in September 1976, the lime subsidy was removed, except for upland improvement and specific farm and horticultural development schemes (BACMI, 1983).
Reductions in the use of lime coincided with a general switch from the use of basic slag (burnt lime) to ground limestone (CaCO₃), which has less than half the neutralising capacity of burnt lime (Boon, Crowther, and Kay, 1988). The basic slag formerly used, is highly caustic and potentially damaging to health. Changes in quantities of lime used may also reflect a shift from remedial liming, where a large initial dose of lime between 5-8 Tons per hectare is applied (dependent on soil chemistry); to maintenance dressings, where smaller quantities of lime, 1 to 2 Tons, are applied in subsequent years to sustain the improvements resulting from remedial liming.

CURRENT STRATEGIES AND PROPOSALS.

As this research is concerned with the effects of liming on moorland and acid organic soil environments, the following discussion is based upon these areas.

Following research on acid rain and the subsequent acidification of surface waters and catchments, the potential of using lime dosing to mitigate the effects of acidification has become recognized. Ormerod and Edwards (1985) suggest that the use of lime dosing on catchments could create a significant increase in the buffering capacity of acid soils against further effects of acidification. They also comment that a further dramatic reduction in the use of lime from 1970 onwards may have contributed to the effects of acidification on surface
waters, the buffering capacity of the soil having been reduced. Their comments are supported by the fact that by the end of the 1980’s the use of lime in the UK had fallen to a level 20% lower than that estimated as required to maintain the current lime status in soils. Consequently, the use of lime is now being promoted once again.

The subsidy for upland improvement was retained in 1976 although at a diminished level and since then, various other schemes have been introduced to promote the use of lime: ADAS and ALPC organised national liming demonstrations; Grant aided agricultural improvement schemes for grassland; E.C. Hill Livestock Compensatory Allowances (HLCAs) for less favoured areas (LFAs), (defined as hill and mountain farms); and ALPC and MAFF strenuously publicise the importance of liming.

As a result of these various activities and subsidies, the liming of moorland and moorland fringes to mitigate acidification and improve pasture, is liable to increase. Selectively though, the grassland improvement scheme does not give grants for; 'any grassland reseeding or regeneration operation on heathland or moorland' as an attempt to preserve these habitats and their ecology.

Coupled with the agricultural necessity of improving acid soils is the use of lime to mitigate acid runoff and acidification of surface waters. The neutralization of
lakes and streams by means of base addition, usually in the form of large doses of lime, has become common practise in Sweden, Norway, and the United States, while experimental programs are under way in Britain, Canada, and Finland, Warfringe and Sverdrup (1988). These programmes have been successful but their effects are only relatively short term, the lime being progressively diluted and removed from lakes and streams by running water. In view of this, research has been initiated to find alternative methods having longer term benefits; one such method, of primary interest to this research, is terrestrial liming which has the potential to neutralize acidic soil water and restore the soil’s buffering capacity. Terrestrial liming and the mechanisms involved in reducing acidification, have been researched by Warfringe and Sverdrup (1988) by use of a mathematical model, the results of which are discussed later.

The control of acidification of surface waters by liming has also been proposed by Water Companies in the UK, involving the addition of lime to reservoirs and by deposit on catchments, applied quantities being similar to those for remedial liming in agriculture. It has also been hypothesised that such methods would reduce colour production on catchments and colour flows in reservoirs. For example, although the direct addition of powdered lime to Llyn Hir Reservoir by Welsh Water, reduced manganese and aluminium levels to near or below EC limits, (the
solubility of these metals being increased by acidification), the effect on colour is less clear. It is possible that the application of lime may have "fixed" colour and made its removal more difficult, (Buckley et al, 1987).

RATIONALE OF THE PROPOSITION THAT COLOUR PRODUCTION AND FLOW MAY BE REDUCED BY LIMING.

High colour levels at treatment works have been found to be associated with low levels of pH in raw waters, and as such it has been proposed that colour production is a function of acidification. Indeed, results from Section 3.1.1. indicate that the majority of colour leached from cores, is leached out in acidic waters. Equally, Mitchell et al, (1990) has shown colour to be negatively related to pH, as the base flows of streams exhibit relatively high pH values and relatively low colour values, compared with peak hydrograph flows of high colour and low pH. From the evidence of natural waters, it has been suggested that increased colour flows may be a result of acidification of catchments and surface waters, by acid rainfall and the decrease in agricultural liming. It has been further suggested, that colour production might be reduced by a decrease in acid rain, and the liming of catchments and reservoirs, thereby reducing acidification. Suggested liming doses being up to 10 tonnes per hectare, necessary to increase the buffering capacity of peat soils
sufficiently to neutralize acid flows, and in turn reduce colour production.

1.2.1. EFFECTS OF MOORLAND LIMING

SOILS AND SOIL WATER.
Warfringe and Sverdrup (1988) developed a conceptual soil liming model, to gain an understanding of the mechanisms involved in terrestrial liming and to develop a tool for planning and evaluation. As part of it they developed a conceptual model of the system of calcite in soils, which is briefly described below. The system is composed of several elements; the soil solution, the gas phase with its components, the soil material with cation-exchange properties, the calcite mineral, and the silicate mineral matrix, which in turn are all subject to chemical weathering reactions in the soil. When calcite is added to the soil it reacts with dissolved species producing two moles of alkalinity and one mole of Ca^{2+} ions for each mole of CaCO_3 that dissolves. These Ca^{2+} ions may then react with exchangeable cations on a solid phase of the soil.
In acidic soils, two chemical reactions proceed in parallel, a dissolution reaction;

\[ \text{CaCO}_3 + \text{H}^+ \rightarrow \text{Ca}^{2+} + \text{HCO}_3^- \]

and a cation exchange reaction,

\[ 2\text{R-H} + \text{Ca}^{2+} \rightarrow 2\text{R-Ca}^{1/2} + 2\text{H}^+ \]

where \( \text{R-H} \) and \( \text{R-Ca} \) represent exchangeable hydrogen and calcium attached to organic matter. The \( \text{Ca}^{2+} \) ions released by dissolution react with exchangeable acidity held on the organic matter, as follows,

\[ \text{CaCO}_3 + 2\text{R-H} \rightarrow 2\text{R-Ca}^{1/2} + \text{HCO}_3^- + \text{H}^+ \]

the hydrogen ions produced may then react with the undissolved calcite in further dissolution reactions. Soil reacidification occurs by the reversal of the cation exchange reaction, \( 2\text{H}^+ \) ions replacing the \( \text{Ca}^{2+} \) ions which then remain in solution.

The rate at which reactions of dissolution and cation exchange occur, between calcium and hydrogen ions, varies between soils and cannot be assumed to be instantaneous. Where dissolution of \( \text{CaCO}_3 \) exceeds cation exchange, the differing buffering systems of the soil solution will determine the response of the soil system to liming. Such buffering reactions in acid soil systems include the protonation of charged aluminium species, the equilibrium reactions of carbonate ions and the dissolution-precipitation of aluminium (a reaction which accounts for the decrease in solubility of aluminium in soils treated with lime).
It is evident from this that the chemical reactions occurring in acid soils are complex and by no means uniform in magnitude or direction and consequently liming needs to be tailored to specific soils, following chemical analysis, to achieve precise effects. As a minimum, Warfringe and Sverdrup's (1988) model included five chemical reaction systems (1) dissolution of calcite in a stagnant aqueous system, (2) cation exchange reactions involving Ca and exchangeable acidity, (3) leaching and accumulation of dissolved components, (4) the CO$_2$-H$_2$O equilibrium reaction, and (5) the Al-H$_2$O equilibrium reaction. Reaction (4) being a limited reaction which occurs in the surface layers of noncalcareous soils, where calcite reacts directly with CO$_2$.

$$\text{CaCO}_3 + \text{CO}_2 + \text{H}_2\text{O} \rightarrow \text{Ca}^{2+} + 2\text{HCO}_3^-$$

As mentioned above the dissolution of calcite has an effect on the rate at which reactions proceed. Dissolution is proportional to the surface area of the limestone particle and the diffusivity of the hydrogen ion in water. The dissolution rate increasing as the solution pH decreases. So, when lime is added to acid peat soils there is a rapid increase in pH, due to dissolution, which then slows considerably as the calcite becomes less soluble in the soil water. At elevated pH levels, above pH 5.5-6.0 calcite is more likely to react with water than the
exchangeable acidity on organic matter particles, in the reaction;

\[ \text{CaCO}_3 + \text{H}_2\text{O} \rightarrow \text{Ca}^{2+} + \text{HCO}_3^- + \text{OH}^- \]

Calcite particles may also become inert in the soil system caused by the "deactivation" of large lime particles due to the presence of precipitates of humus and clay minerals, which can clog the surfaces, Sverdrup and Warfringe (1985). The effects on dissolution demonstrate that finely divided limestone is more chemically active and less likely to become inert, so smaller quantities are required to be effective. From their model, Sverdrup and Warfringe (1988) calculated that to mitigate acid runoff and in turn, the acidification of soils:

(i) the calcite dose must exceed the exchangeable acidity of the soil

and

(ii) the limestone product used does not need to have a lognormal particle size distribution finer than 0-1mm.

Many other liming projects have been recorded by various researchers, as the potential of terrestrial and lake liming to mitigate the effects of acidification becomes realised. The effects of liming on pH and aluminium levels are well documented (reported) however, little direct
comment has been made on the overall effects on water quality and especially the effects on colour generation. The effects on ecology are also less well documented, although they have been researched at some sites the results are as yet unpublished. Davis and Goldstein (1988) using a Integrated Lake Watershed Acidification Study (ILWAS) begun in 1977, compared the effects of terrestrial liming with that of direct water body liming. Their research centred around Woods Lake Watershed in the Adirondack region of New York State and the use of several simulated models of liming strategies. They concluded that, direct applications of lime to lakes resulted in an immediate increase in lake outlet pH and alkalinity, but that the effects were only short term as the lime is quickly flushed through the aquatic system. Terrestrial liming however was characterized by a lower magnitude, more gradual, effect to both the lake outflow and soil pH and alkalinity, attributable to base saturation of the acid exchange sites in the soil. Such effects being of long duration as alkaline material was not readily removed from the soil system.

Addition of lime directly into the lake increased the original pH from 4.5 to 10.0 but as the lime mixed, a stable level of pH 7 was reached, reduced acidification lasting 4 years. Soil pH's showed less dramatic increases, from pH 4.8 to 6.0 but these were maintained for much longer. Simulations indicated that reacidification had not
occurred by the twelfth year, and the effects over an unlimed plot were still present 99 years later, although differences were small, 0.3 of a pH unit. This suggests that the addition of lime can provide a long term buffering capacity to catchment soils which is reflected by the pH of surface waters.

One further observation which arose from the model simulations, was that the deeper soil layers on limed catchments did not receive significant quantities of lime leached from above. Only in the upper layers did the applications appear to increase base saturation significantly. This factor is noteworthy when considering whether colour is reduced by liming.

Donald and Gee (1992), report on the Llyn Brianne Project, mid Wales, where liming of small streams by a variety of catchment liming techniques has occurred, including agricultural source areas, agricultural improvement i.e. ploughing; and application of fertiliser. Soils were brown podzols, stagnopodsols and peats supporting moorland grass and conifer plantation. Liming of land marginal to streams, excluding hydrological source areas, was found to be largely ineffective, pH continued to range from 4.8 to 4.6 and filterable aluminium remained high, whilst other sites which included the liming of hydrological source areas at rates of 25t ha⁻¹ were successful, suggesting that to mitigate acidification whole catchments must be limed.
The consequences of this on colour generation in the catchment are not reported although Llyn Brianne is known to have discoloured waters, Buckley et al (1978).

The researchers report from the literature that liming has both aquatic and terrestrial effects which include:- increased numbers of sediment bacteria, increased rates of decomposition in sediments and reductions in the growth and distribution of sphagnum, but comment that no evidence for this has been found at Llyn Brianne, although this has yet to be reported. Donald and Gee emphasise that liming is likely to be a component of any remedial strategy in the next 30 years until emission reductions greater than those proposed by forthcoming E.C. Directives are implemented. A factor which requires the "full" effects of liming to be realised.

Jenkins et al (1991) report comparable results at Llyn Brianne identifying the liming of source areas as the most effective method of mitigating acidification.

Diamond et al (1992), report contrasting results from a terrestrial liming project on a catchment scale at the river Esk, NW England at a dosage of 5t ha⁻¹, (a fifth of the dosage at Llyn Brianne) and report that there was little evidence to support that liming had a major impact on water chemistry. However, the mean concentration of total humic substances was measured and was found to drop
sharply during the first liming from 1.3 to 0.87 mg litre$^{-1}$ and then to increase to 1.19 mg litre$^{-1}$. It should be noted however, that liming occurred at a time when seasonal levels of colour are normally at their lowest and that decreases and increases in colour were due to seasonal fluctuations in the "natural" colour cycle. Liming (at 5t ha$^{-1}$) in this case appears therefore to have neither reduced nor increased colour.

Two acid lakes in West Wales, Llyn Hir and Llyn Berwyn were treated with 2.5 and 12t of lime respectively. The resulting pH increases from 4.2 to 6.9 and 4.8 to 7.0, have been investigated and reported by Underwood et al (1987). The catchments comprised peaty gleyed podzols and amorphous peat and were reported to have problems of water discoloration, Buckley et al (1987). Changes in pH following liming have resulted in metals formerly held in solution being precipitated and deposited on the lake bottom, where acid stream water mixes with neutral lake water. The precipitation reactions of both aluminium and humic substances removing bicarbonate from solution and reducing pH, in the case of Llyn Berwyn pH fell to 5.5 more rapidly than predicted, possibly because of the above reaction. Again, it is difficult to isolate this increase in pH from "natural" variations in colour because humic acid levels rose steeply owing to the influx of humic acids from streams in 1984/85 as a result of the 1984 drought; colour rose from a mean of 1.4 mg litre$^{-1}$ to 7.2 mg litre$^{-1}$. 
A trend which was also observed in other Welsh catchments with thick peats.

This reaction is reversible (Sverdrup and Warfringe, 1985) and consequently metal humic sediments may be remobilised if lakes are allowed to reacidify, potentially degrading water quality to levels lower than those before liming. Further dissolution of limestone from the lake bed is inhibited by metal-humic complexes on particle surfaces, resulting in particles becoming inactivated, which requires lakes to be re-limed after only a few years; Llyn Berwyn was re-limed 212 days and Llyn Hir 255 days after the first application.

Contrasting studies by Adams and Evans (1989), have indicated that aluminium levels are increased by liming and they have also noted its effect on colour. Topsoils were examined to investigate the effects of liming on soil properties and streams draining catchments analyzed for total anions and cations, including examination of the concentration of various aluminium species. Studies on the influence of soil properties on stream water chemistry were supplemented by the analysis of leachates from soil columns (catchment soils comprising peaty gley podzols, brown podzolic soils and peaty gleys) leached with simulated rain water, in the laboratory. After 12 leachings the mean pH for unlimed soils equalled 4.03 and for the limed soil was 6.30, whilst mean colour equalled 0.26 Abm⁻¹ and 0.73 Abm⁻¹
respectively, measured at 225 nm. This indicates that colour levels will increase with pH. Total aluminium measured by atomic absorption spectroscopy was greater in leachate from limed soil, most of the aluminium in the limed soil not being acid reactive. Although greater amounts of organic matter were leached from the limed soil the author states "it is not clear whether the bulk of the acid-unreactive aluminium was associated with organic matter". Of the total monomeric aluminium measured, the content for unlimed cores inorganic was 63% and organic 37%; whereas for limed cores the inorganic content was 4% and the organic content 96%. The effects of soil pH and the speciation of Iron appearing in drainage waters was also found (from catchment studies) to be important, limed soils exhibiting greater quantities of non-cationic than cationic Iron, the reverse being indicated for unlimed soils.

Similar effects have also been noted by Kreutzer et al., (1989), when comparing the acid irrigation of a Norway Spruce stand before and after liming, at a dose of 4t ha⁻¹. Liming led to a significant increase in dissolved organic carbon, which was associated with the mobilisation of metals such as Lead, Copper, Iron and Aluminium in organic complexation. Nitrification also increased in the surface humus layer, causing nitrate concentrations in the seepage water to exceed 250 mg NO₃ litre⁻¹ (W.H.O. limit equalling 11.3 mg litre⁻¹ for potable water). Increases in dissolved
organic carbon (DOC) resulted from increased hydrolysis in humic layers, a large part of these DOC substances forming metal organic complexes, it is understandable therefore that aluminium and heavy metals increased in the soil solution.

Marschner et al., (1989) found similar increases to those reported by Kreutzer et al., (1989) but rather than metals being mobilised, they were found to accumulate. An experimental plot was dosed with lime at 6.1t ha⁻¹ and with fertiliser (K₂SO₄) at 145kg ha⁻¹. This lead to a significant increase in pH and base saturation in the top 10cm of a mineral soil after 2 years, the upper 5cm of which was organic forest floor, classed as raw humus moder. Data on elemental fluxes gives evidence for increased mineralisation rates, enhanced heavy metal accumulation in the forest floor and increased soil solution concentrations of potentially hazardous substances, for example NO₃ following the stimulation of nitrification. Al and Fe had low output attributed to precipitation or reduced dissolution at higher pH, the pH having risen from 4.0 to 6.8.

Clearly from the above studies, the use of lime to mitigate acidification may ameliorate some water quality problems, notably that of aluminium toxicity, but it may create others. Consequently the use of lime as a water quality management tool should be considered carefully.
HUMIC AND FULVIC ACIDS

In the terms of organic chemistry it has long been recognized that the solubility of humic substances increases with increasing pH. In fact, the most efficient and most widely used extractant for humic substances in soils is dilute aqueous NaOH, (Schnitzer and Khan, 1978). The chemical nature of organic colour in water follows a similar trend. The extent of colour extraction being dependent on pH, colour molecules showing acidic properties, evidenced by their pronounced solubility when extracted by alkali, such solubility intensifying colour chemically, upon the addition of a base. The pH relationship with colour is not linear or uniform, as coloured waters from different sources have different relationships. This is attributed to differences in phenolic acidity and structural complexity, Christman and Ghassemi (1966).

It could be thought however, that these laboratory effects might not occur in the natural environment due to the multitude of chemical and biological reactions occurring in the soil. Indeed this is supported by the evidence of colour to pH relationships observed at Treatment Works and experiments in the field and laboratory. Against this however a review of the literature gives weight to the former case.
Hay, James and Vanloon (1985) studied the effects of acid rain on solubilisation of organic matter. Cores of Canadian Shield podzol at depths of 10 and 20 cm were leached with aqueous solutions of pH 5.7, 3.5 and 2.0, the resulting leachate being measured for concentration of total organic carbon, total carbohydrate, fulvic acid and ammonium — plus amino-nitrogen (AAN). Cores were leached under simulated rainfall over 16 days, equivalent to one year’s precipitation. Results showed that the highest concentrations of total organic carbon, total carbohydrate and fulvic acid were generated by the core leached at pH 5.7 and at 10 cm depth as opposed to 20 cm. The core leached at pH 2.0 dissolved the least amounts of these components. Fulvic acid was determined by the absorbency of a standard compared with that of a sample, measured at 300 nm in 1.0 cm cells by spectrophotometry, and converting into $E_4/E_6$ ratios, such measurements being comparable to those of ‘colour’. Measurements of AAN followed an opposite trend to those mentioned above, perhaps indicating an increase in microbial activity with increasing pH. The soils also exhibited considerable buffering action in regulating leachate pH.; the solubilization of organic acid and cation exchange processes acting as buffers.

The solubility of colour related to pH in soil systems has also been investigated and modelled by Tipping (1987). The aim was to relate the dissolution of humic substances to the physio-chemical properties of acid soils. A model was
formulated to predict the effect of changing environmental conditions on the levels of coloured material in the soil solution, attention being given to the effect of acid rain. Initially, soil suspensions containing 2.5g of dissolvable humic substances (HS) were titrated with acid or base to give pH values in the range pH 3-5. Findings, as did those of Christman and Ghassemi (1966), indicated that for a given soil the concentration of HS passing into solution increased with pH, but the precise relationship and magnitude varied from soil to soil. The amount of dissolution representing only a small proportion, 3%, of the total HS present. To overcome the problem posed by the varied relationships between pH and colour, the net humic charge of HS was calculated and plotted against the amount of HS in solution (mg/l), by which a much more uniform relationship was obtained. The solubility of the HS was governed by their net electrical charge, solubility increasing with increasing charge. As noted previously, when soils are treated with NaOH, nearly all the HS is extracted, whereas at low pH levels, solubility is much lower but still sufficient to colour water. Net charge of HS in alkali being very high, 5-10 meq gHS⁻¹, whilst in acid the charge is much lower, < 1 meq gHS⁻¹, Tipping (1987).

From the relationship between colour and net humic charge, a model was produced to predict colour levels in soil solutions by CHAOS (Complexation by Humic Acids in Organic Soils) and took into account (1) the complexation by soil
HS of protons, (2) the cation exchange capacity of Al and Ca\(^{2+}\) ions and (3) a description of the distribution of ions, between the diffuse double layer surrounding the soil particles and the bulk solution, both inorganic and organic elements being calculated. HS dissolve when the surface of the soil particle and the diffuse double layer pass into the aqueous phase, i.e. the soil solution. Results from CHAOS have so far predicted that if the acidity of precipitation decreases (the original motivation for the model), the magnitude of the negative charge on the soil HS would increase, resulting in the generation of high colour values in soil water. The predicted effect is obviously parallel to that caused by the addition of lime to soils.

Mitchell (1990), comments that many authors have noted increases in the transparency of lakes following acidification, attributed to the input of cation acids, both in the form of inorganic aluminium species released by cation acids and inorganic aluminium species released by watershed acidification. Two mechanisms are involved; co-precipitation of humic substances with aluminium hydroxide, resulting in the reduction of dissolved organic matter, colour. Secondly, colour is reduced, by the alteration of spectral properties of dissolved humic substances, by the cleavage of high molecular weight humics (high colour) to low molecular weight humics (low colour) but there is no overall decrease in dissolved organic matter. These mechanisms suggest that on the reduction of
acidification by the addition of lime, the above processes would be reversed and colour would increase.

Finally, as a result of solubilisation and dispersion of humic compounds due to the addition of lime, the stability of organic matter is decreased, exposing fresh surfaces and increasing the availability of organic matter to microbial attack, these processes being further discussed by Raven and Arimimelech (1978).

MICROBIAL POPULATIONS AND DECOMPOSITION RATES. Wakesman and Purvis (1932) commented that although in the past, peat has been assumed to be a sterile medium, this was not the case. In fact, microbes are found in certain moorland acid peats, not only present in the surface layers but also at depth and in some cases there may be an increase in numbers with depth. Bacteria found at these depths seem to comprise largely of specific types, capable of growing in acid (pH3.8-4.0) media, and apparently capable of living both aerobically and anaerobically. Decomposition in such peats is slow however, owing to the adverse soil environment, (acidic and anaerobic) and the nature of the organic matter to be decomposed; the cellulose, hemicellulose and carbohydrates (from Sphagnum) being highly resistant to decomposition. Wakesman and Purvis (1932) demonstrated that the low numbers of cellulose-decomposing bacteria occurred largely because the soil pH was 4.0 or less, and therefore highly unfavourable
to their growth. Peat samples of above pH 4.3 revealing significant increases in microbial activity, numbers of bacteria (per 1 gram of moist material) equalling 766,000 at 75cm pH 3.9 and 2,260,000 at 195cm pH 4.2, peat sample from Denbo Heath, Maine, New Jersey; an indication of the potential of peats to increase bacterial numbers if soil conditions become favourable.

As discussed previously such favourable soil pH conditions, can be produced by the addition of lime, the results of which are now discussed.

Farrell and McDonnell (1986) observed decomposition rates in man modified peat soils as part of a study to look at the reclamation of cutover peat on permanent grassland in Ireland. Their study looked at the decomposition rates of organic matter when mixed with mineral soil (with a high CaCO₃ content) compared with the influence of applied lime. Decomposition rates being measured by incubating peat, with either mineral soil or lime (pH 5.5), CO₂ evolution representing decomposition as mg C evolved per gram dry matter of peat. Results indicated that soil added treatments evolved significantly more CO₂ than limed treatments at earlier stages, but by weeks 11 and 12 the greatest amount of evolution occurred in the limed treatments, cumulative totals at the end of the period being approximately equal. In both cases the treated peats showed significant increases in decomposition over that of
the control, which indicated an amelioration of the environment for microbial metabolism.

Abrahamsen, Hovland and Hagvar (1980) studied the effects of acid rain and liming on soil organisms and the decomposition of organic matter, organisms including fungi, bacteria and invertebrate animals. Their findings indicated that most invertebrates seemed to tolerate and even prefer, more acidic conditions, to those occurring naturally (pH4.5). In agreement with this, very few animals became more abundant when soil acidity was reduced by liming. Decomposition studies showed that acidification had little effect on the initial decomposition of plant remains (fresh). However, experiments concerned with incubation of raw humus material indicated that the decomposition of humic material is pH dependent, the effect of liming increasing carbon turnover. The opposite is true of acidification, as decomposition rates decrease significantly with increased acidification of humus material.

Maltby (1979,1984), studied the effects of liming as part of a study looking at the response of soil microflora to moorland reclamation. Reclamation being in the form of ploughing which improves drainage and aeration; the application of lime and slag which improves nutrient status and ameliorates acidity; and - reseeding. Four groups of micro-organisms were studied; bacteria, actinomycites,
filamentous fungi and yeasts, and numbers estimated using the soil-dilution plate method. The study sites included: (1) an area reclaimed in June 1974 which was sampled one week after ploughing before any addition of chemicals (including lime); (2) a site sampled nine months after ploughing and the application of carbonate lime and basic slag (at 5.0t and 1.2t/ha respectively); and (3) a site reclaimed in 1845-48, then reploughed and reseeded in the 1940's and again in 1976, carbonate lime and basic slag being applied on both occasions and in 1966, at the above rates. Unreclaimed sites provided the control measure, soils consisted of stagnapodzol, and stagna humic grey.

Results from Site 1, showed dramatic increases in microflora, 'total' CFU's (colony forming units) from surface horizons exceeding, by up to two orders of magnitude, the figures obtained at comparable depths from the unreclaimed profile. Bacteria proliferated far more than for other groups, the increase at 0-2cm being from $3.52 \times 10^6$/cm$^3$ (unreclaimed) to $645.02 \times 10^6$/cm$^3$ (reclaimed). Without liming, pH increased slightly from below 4.0 to 4.5, in the ploughed layer.

At Site 2, the differences in 'total' CFU's showed a similar pattern but with an extended depth range. Bacteria, actinomycetes and filamentous fungi all increased significantly whilst yeasts exhibited no significant change. Intact, but inverted peat horizons supported very
significant increases, especially in numbers of bacteria and actinomycetes. Additions of CaCO$_3$ and basic slag having produced a very large increases in exchangeable Ca and pH, (to beyond 6.0).

The final site, Site 3, demonstrated large increases in bacteria, actinomycetes and yeasts. Relatively high numbers of actinomycetes produced consistent increases in their ratio to bacteria as did their proportional representation, compared with unreclaimed soil. At pH 6.0 the reclaimed site exhibited markedly higher pH than the unreclaimed and reverted sites.

From the above study it is difficult to isolate the effects of liming from those of ploughing, it is clear however, that the effects on different groups of micro-organisms are broadly similar. This seems to point to the influence of general environmental conditions rather than to specific factors, which would be expected to affect groups and patterns differently. Nevertheless, increases in group numbers do closely follow increases in pH, and group patterns by depth are very similar to pH patterns by depth, the greatest changes being due to lime dosing. Increased numbers of actinomycetes in reclaimed soils were identified, a factor which probably has decomposition consequences for peats which have been limed.
Actinomycetes include species capable of breaking down highly complex organic substrates, for example, cellulose and hemicellulose, but they are not generally thought to be capable of inhabiting waterlogged soils in large numbers or being effective substrate colonisers below pH5, although evidence does exists for acidophilous types in these conditions, Williams, Davies, Mayfield, Khan, (1971), . Therefore, the amelioration of acidity by the addition of lime, combined with the correct moisture conditions, could lead to an increase in decomposition of organic matter subsequently resulting in increased colour flows. This theory is supported by increases in mineralisation in reclaimed soils, where peaty horizons have contributed to the development of brown-earth line horizons, on Exmoor, Maltby (1984).

The effects of liming and drainage on decomposition rates, has also been considered by Bridgham et al., (1991) by the use of cellulose cotton strips, decay being related to the loss of tensile strength within the strips. Research showed that agricultural stress (on disturbed peatland), that had been drained, limed and fertilised, had much higher cellulose decay rates than undisturbed peatland, decay rates being up to 9 times greater. Again it is difficult to separate the effects, but Bridgham comments that liming of undisturbed peat did not increase decomposition. Although he emphasises that the high pH
resulting from liming cannot be ruled out as a factor leading to increased decomposition.

The effects of acid rain on micro-organisms has also been discussed by Rechcigl and Sparks (1985). They reached the same conclusions as above, namely that acidification causes a general reduction in the population of bacteria and actinomycetes and also causes decreased rates of humus decomposition; conversely, the reduction of acidity by liming promotes decomposition of humic compounds. As demonstrated by Kreutzer et al., (1989), deacidified soil horizons show a marked increase in the activity of bacteria, including chemolithotrophic nitrifiers and cause sharp increases in nitrate concentrations in the soil solution.

1.3. BACKGROUND AND COMMENTS FROM THE LITERATURE ON DITCHING.

Reclamation of blanket bog by drainage is increasing and the subsequent loss of upland heath vegetation has been documented by Parry et al, (1981). The principle of drawing down the water table by drainage is of interest to several forms of development or reclamation: forestry; pasture improvement for agriculture; and promotion of heather for grouse moors. The practice also has consequences in terms of water quality, in this case colour production.
Drainage initiates the processes which increase colour production by drawing down the water table aerating the surface of the soil. The effects of increased colour production owing to ditching are clearly visible in the Howstean catchment study, referred to in Sections 3.0. and 4.0., colour levels being especially high in sub catchment 13 (HS 14) where high density ditching occurred in 1984. Mitchell et al, (1990), have noted similar effects on drained catchments in catchment studies at Roundhill and Leighton Reservoirs, N. Yorkshire. Sampling of waters from Llechweddwmawr by Welsh Water has revealed greater quantities of humic acid in water flowing from forest-ploughed moorland than from a moorland control area, Buckley et al, 1987.

Three main effects of drainage influence the production of colour:–

(i) Water table fluctuations
(ii) Enhanced microbial activity
(iii) The removal of increased amounts of sediment.

These effects and their consequences are mostly similar to those of liming and burning and as such have largely been discussed previously in Section 1.1. and 1.2. Therefore further comment is brief.
WATER TABLE FLUCTUATIONS

Early studies by Conway and Miller (1960) compared flow characteristics of ditched and non-ditched catchments at the Moor House National Reserve in Northumbria. Drained catchments were found to have very sensitive response times to rainfall, peak flow rates often being reached 15 or 30 minutes after peak rainfall rates and they subsided just as quickly. The storage capacity of drained catchments being reduced, the effects of rain lasted only a few hours before pre-rain levels were restored. Undrained catchments exhibited smaller rates of flow with delayed peak flow response times. The greater storage capacity of the undrained catchments lead to longer duration effects, slightly enhanced flows being maintained for days. Reduction of natural storage capacity was further demonstrated in that summer flows from drained areas ceased earlier than those from non-drained areas.

More detailed studies by Robinson and Newson (1986) have revealed similar catchment trends. Their studies were based on the River Severn and River Wye upland catchments and compared the hydrology of natural blanket peats to those that had been ditched and forested. Flow patterns revealed that those drained catchments (peat and mineral soil) which supported forest, had flow patterns which exhibited large fluctuations either side of the mean flow, which ceased altogether for up to 30% of the study period; all characteristic of rapid hydrological events. This was
distinct from the undrained deep peat catchments which showed relatively little fluctuation about the mean flow, none of which ceased during the study period, indicating more gradual hydrological events. Further evidence, supporting the rapid run-off response and increases in peak flows, being given by Robinson (1980).

The duration of the above changes in flow pattern and the subsequent fluctuations in soil water tables depends on land use, the type of ploughing/ditching and the nature of the peat/subsoil. The establishment of forest for example, may reduce peak flows to below those of undrained moorland, due to the effect of mature trees on the water balance of catchments. Whereas peat, which has been ditched to improve pasture or promote heather growth, may exhibit the effects of increased peak flows and diminished water tables for an infinite period. The magnitude and duration being dependent on the type of ploughing/ditching whether hard or soft and the rate of erosion, coupled with rate of sediment removal. ('Hard' ploughing consisting of furrows/ditches on steep gradients with drains leading straight into the streams and 'soft' ploughing consisting of furrows/ditches following contours with drains stopping short of streams.) 'Hard' ploughing is more likely to be associated with rapid erosion rates, coupled with increased sediment removal, which deepens ditches and increases the draw down of the water table; whilst 'Soft' ploughing is more likely to be associated with erosion, coupled with low rates of sediment
removal, which may block and eventually refill ditches, raising the water table once again.

Water table patterns have been shown largely to reflect surface topography, rapid changes in topography lower the water table accordingly, due to the low hydraulic conductivity of peat. Ditching can therefore draw down the water table on either side of a ditch and even between ditches, depending on depth and density. Robinson and Newson (1986) observed water tables either side of ditches on the upper River Severn catchment and found that, although water tables sloped towards ditches from even the most distant sampling points (in this case bore holes), the effects were slight and the draw down around the drains was largely restricted to about one metre from the drain on each side. This reflected the very low hydraulic conductivity of peat below the surface layers. Coulson et al., (1990) also recorded water table fluctuations between "soft" ploughed ditches, the water table being at its lowest immediately down gradient from the ditch. However the level of draw down varied from site to site, the difference in the position of the water table 1.5 m up gradient from the ditch and midway between the ditches was only 3.3mm at one site, Moor House, Cumbria, whilst at the other, Waskerley, Durham, differences amounted to 107mm. Decreases in water content between differing sites equalling 2% and 25% respectively. Similar trends in naturally dissected peats were also observed as studies of
water table fluctuations within peat hags, indicated a mirroring of the surface shape by the water table.

Water levels between hags were found to differ depending on the size, those less than ten metres diameter exhibited steeply declining water levels, water table draw-down being apparent in the central part of these small diameter hags. Further erosion causes lowering of the water table so that it falls below the level of the hag and exposes the peat to oxidation resulting in the production of colour.

Where high density ditching takes place, this sequence is almost certainly the same, especially where erosion has cut the base of the drain through the peat to the subsoil, or the surface geology. Water table fluctuations have also been related to increased solute release from peatlands. Peat hydraulic conductivity is critical in determining the volume of peat affected by drainage; in amorphous peats with low hydraulic conductivity the water table draw down may be confined and hence the source of solutes reaching the ditch is small; whereas in fibrous peats, the volume affected and hence the potential source of solutes, may be much greater owing to a relatively higher hydraulic conductivity. The relative effects of these differences being governed by ditch density and depth.

Heathwaite (1989) and (1991), studied solute release from drained and undrained peat by incubation and leaching in
Undrained peat was found to have a higher rate of and total amount of solute release than peat that had previously been drained. The conclusion was that drainage would release high solute concentrations from peat masses and that a large proportion of solutes had already been lost, presumably via drainage ditches. These findings were applied to field studies in areas of pump drained fen peat. Studies revealed that the potential for solute release was high and that pump drainage leads to a cycle of aeration of the peat, initiating chemical and microbial transformations, followed by water logged conditions resulting in solute release and transfer, once pumping is re-initiated. These conditions being similar to wetting and drying cycles (Birch 1958 a&b). Although Heathwaite does not measure colour in his study he reports that coloured waters have lead to problems in analysis, although colour levels were relatively low and comments that in base rich peats, organic acid export is likely to be low owing to internally generated alkalinity; inferring that colour loss in acid peats would be much higher. Comment is also made on the potential of peat drainage to lead to water course pollution; as water table fluctuations accelerate nutrient release through increased microbial activity. Nitrate losses are higher in soils which fluctuate between aerated and water logged conditions than in those which are either permanently water logged or aerated.
Solute release from the peat was not simultaneous, physico-chemical reactions within the peat and hydrological control were found to affect the rate at which solutes entered the drainage ditch from the peat.

Ditching can therefore be expected to increase water table fluctuations compared with undrained moorland, owing to the rapid response times of hydrological events and the subsequent drawing down of the water table. This creates aerobic conditions in peat layers above the water table as well as increasing the number of wetting and drying cycles, thereby initiating the processes responsible for increased colour production.

**ENHANCED MICROBIAL ACTIVITY.**

Although this has been previously discussed the work of Birch (1958), Maltby (1979), (1980) and (1984), and Wakesman and Purvis (1932) is of particular note.

Further discussion by Dickinson and Dooley (1967) concerns the microbiology of cutaway peat. Undrained basal peat was found to support small populations of micro-organisms, with restricted activity due to poor soil conditions. Upon exposure of the peat, the populations of bacteria, streptomycetes and fungi increased owing to improved soil conditions. These conditions are likely to be produced on the sides of ditches; this may seem a relatively small scale effect, but ditch sides can represent a large surface
area of exposed peat, even small peat samples can produce large amounts of colour for extended periods, as will be shown later.

Decreases in soil moisture as a result of ditching have been shown to increase microbial activity. Coulson et al., (1990), measuring the rate of cellulose decomposition at different distances above and below ditches. Lowering of the water table allows greater penetration of oxygen below the surface and lowers the depth of the anaerobic zone, where there is little decomposition. This results in increased decomposition, which was found to be higher on the up slope side of the ditch than on the down slope side (contour ploughing). Decomposition was measured using cotton strips and found to be greatest at sites where ditching had reduced soil moisture significantly. At the Moor House site the loss of tensile strength declined from 57% at 80mm to 14% at lower levels, whereas at Waskerley losses declined from 67% to 35%, the decomposition rate being higher not only in the surface layers at Waskerly than Moor House, but also extending to greater depth, giving an overall higher rate of decomposition of 70%.

These findings are confirmed by the work of Bridgham et al., (1991), in their comparison of decay rates in natural and disturbed peatlands, decay rates being up to 9 times greater at disturbed sites. A number of sites were studied on Pocosins (wetlands) having 1-3 m thick peat deposits,
the loss of tensile strength in cotton strips being used to assess decay rates. Sites included undisturbed, drained, drained and forested and agricultural sites. Decomposition increased at all sites, drainage relieving excessive soil moisture and the resultant aerobiosis being the dominant factor explaining these increases. Decay rates were found to be 10% at undisturbed sites, whilst drained sites had rates of up to 80%, drainage increasing decomposition at some sites despite nutrient conditions being similar to undisturbed sites. Decay rates decreased with depth at all sites suggesting that water logging was not the only factor governing decay rates, a decrease in soil fauna with depth partially explained this, soil temperature, pH and the availability of nutrients being secondary factors.

The effects of drying can also decrease the stability of organic matter and lower its resistance to microbial attack. These drying effects are discussed in Section 1.1.2.

SEDIMENT REMOVAL
Extensive drainage of upland catchments is known to increase sediment yields. Robinson and Blyth (1980) demonstrated that over the first five years the drainage of a small upland catchment resulted in sediment yields equivalent to nearly half a century's load at pre-drainage rates and in subsequent years sediment yields, remained at four times pre-drainage levels.
Sediment removal leads to the exposure of fresh surfaces, causing rapid increases in microbiological activity. Following erosion, removal can deepen and widen ditches, increasing the effect on the drawing down the water table. In some cases ditches cut right through the peat to the subsurface which lowers the water table significantly. In short, sediment removal exacerbates the effects of drainage by deepening ditches and further lowering water tables, whilst lack of sediment removal can reduce these effects, by blocking drains, thereby returning the water table towards its previous level.

1.4 BACKGROUND PEDOLOGY

CLASSIFICATION AND DESCRIPTION
As large proportions of the research sites used are covered with deposits of peat there follows a description indicating its definition, origin, classification and distribution.

Peat is an unconsolidated black or dark brown soil material consisting largely of slightly decomposed fibrous vegetable matter that has accumulated in a waterlogged environment which is anaerobic. It is formed under cool, humid climatic conditions and in post glacial times there were lengthy phases of peat growth during the Atlantic period, Sub-Atlantic period and the Turbarian periods in Scotland.
The majority of peat vegetation creates acid conditions with sphagnum moss as the dominant species, creating blanket and raised bog (Dictionary of Physical Geography 1984). Alkaline or neutral peat can also be formed in base-rich environments such as fen or carr, but these are not relevant to this study and are not discussed.

Peat is classified in several different ways, by its degree of humification, see Table 1.2; its nutrient status; the vegetation or plant species from which the peat was formed and whether or not the material was formed in situ. For example, nutrient rich peats are designated as eutrophic but nutrient poor peats are oligotrophic. Eriophorum peats are mainly formed from cotton grass, *Eriophorum vaginatum*, Sphagnum peat by *Sphagnum*. Autochthonous peats are formed in situ while allochthonous peats are formed from transported organic debris.

Peat is mapped and defined slightly differently by the Soil Survey of England and Wales (SSEW), the Forestry Commission and the Geological Survey. The S.S.E.W. defines 'Peat Soils' as "primarily organic soils derived for the most part from decomposed plant remains that accumulated under waterlogged conditions, either as autochthonous peat or as constituents of sub-aquatic sediments such as organic lake muds" (Avery 1980). The survey then subdivides peat soils on the basis of the state of humification, based mainly on fibre content and nutrient status, see Table 1.3. For
mapping purposes, the survey recognises peats, where the layer is thicker than 40cm. rather than merely peat-surfaced mineral soils.

The Forestry Commission classifies peat with emphasis on the nutrient status, nitrogen being of greatest importance. The peats are classified mainly on the basis of their associated vegetation. The F.C. and Geological Survey defined and map soils as peat, where the surface organic layer is greater than 50cm.

FORMATION OF PEATS

Peat accumulates when plant production is not in equilibrium with the decomposing plant material, i.e. production is greater than decomposition. Maltby (1986), described peat formation as follows: - "When plants die they begin to decompose. With the help of microbes, the plant tissue oxidises, eventually into carbon dioxide and water. Where low temperatures, high acidity, low nutrient supply, water logging and oxygen deficiency retard decomposition, the plant matter does not oxidise, but instead accumulates and is transformed into peat."

The rate of decomposition determines whether or not peats continue to accumulate or begin to diminish. Rate of decomposition is determined by several inter-relating factors, the quality or characteristics of the plant matter, the population of soil animals and micro-organisms.
Table 1.2
A MODIFIED VERSION OF THE VON POST SCALE FOR ASSESSING THE DEGREE OF DECOMPOSITION OF PENT (FROM AVERY 1980)

<table>
<thead>
<tr>
<th>Degree of decomposition</th>
<th>Nature of liquid expressed on squeezing</th>
<th>Proportion of pent extruded between fingers</th>
<th>Nature of plant residues</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>81 Clear, colourless</td>
<td>None</td>
<td>Plant structure unaltered; fibrous, elastic</td>
<td>Undecomposed</td>
<td></td>
</tr>
<tr>
<td>82 Almost clear, yellow-brown</td>
<td>None</td>
<td>Plant structure distinct; almost unaltered</td>
<td>Almost decomposed</td>
<td></td>
</tr>
<tr>
<td>83 Slightly turbid, brown</td>
<td>None</td>
<td>Plant structure distinct; most remains easily identifiable</td>
<td>Very weakly decomposed</td>
<td></td>
</tr>
<tr>
<td>84 Strongly turbid, brown</td>
<td>None</td>
<td>Plant structure distinct; most remains identifiable</td>
<td>Weekly decomposed</td>
<td></td>
</tr>
<tr>
<td>85 Strongly turbid, contains a little pent in suspension</td>
<td>Very little</td>
<td>Plant structure clear but becoming indistinct; most remains difficult to identify</td>
<td>Moderately decomposed</td>
<td></td>
</tr>
<tr>
<td>86 Muddy, much pent in suspension</td>
<td>One third</td>
<td>Plant structure distinct but clearer in the squeezed residue than in the undisturbed pent; most remains unidentifiable</td>
<td>Well decomposed</td>
<td></td>
</tr>
<tr>
<td>87 Strongly muddy</td>
<td>One half</td>
<td>Plant structure indistinct but recognisable; few remains identifiable</td>
<td>Strongly decomposed</td>
<td></td>
</tr>
<tr>
<td>88 Thick mud, little free water</td>
<td>Two thirds</td>
<td>Plant structure very indistinct; only resistant remains such as root fibres and wood identifiable</td>
<td>Very strongly decomposed</td>
<td></td>
</tr>
<tr>
<td>89 No free water</td>
<td>Nearly all</td>
<td>Plant structure almost unrecognisable; practically no identifiable remains</td>
<td>Almost completely decomposed</td>
<td></td>
</tr>
<tr>
<td>90 No free water</td>
<td>All</td>
<td>Plant structure unrecognisable; completely amorphous</td>
<td>Completely decomposed</td>
<td></td>
</tr>
</tbody>
</table>

Table 1.3
THE PENT CLASSIFICATION OF THE SOIL SURVEY OF ENGLAND AND WALES (FROM AVERY 1980)

<table>
<thead>
<tr>
<th>Major group</th>
<th>Group</th>
<th>Subgroup</th>
</tr>
</thead>
<tbody>
<tr>
<td>10 Peat (organic) soils</td>
<td>10.1 raw peat soils</td>
<td>10.11 raw oligo-fibrous peat soil</td>
</tr>
<tr>
<td></td>
<td>Without earthy topsoil or ripened mineral surface layer</td>
<td>10.12 raw oxyfibre peat soil</td>
</tr>
<tr>
<td></td>
<td>10.2 Earthy peat soils</td>
<td>10.13 raw (unripened) oligo-amorphous peat soil</td>
</tr>
<tr>
<td></td>
<td>with an earthy topsoil,</td>
<td>10.14 raw (unripened) autro-morphous peat soil</td>
</tr>
<tr>
<td></td>
<td>or a ripened mineral</td>
<td></td>
</tr>
<tr>
<td></td>
<td>topsoil overlying</td>
<td></td>
</tr>
<tr>
<td></td>
<td>organic material</td>
<td></td>
</tr>
</tbody>
</table>
and the environmental factors such as temperature and moisture content. Characteristics of plant litter which influence decomposition include the number of nutrients available, base cations and the resistance of certain long chain organic molecules such as polyphenols and lignins. Higher temperatures allow decomposition to occur more rapidly than low temperatures, but moisture is required. However, too much water as in waterlogged anaerobic conditions, limits decomposition to a slow rate. Soil microfauna and micro-organisms are vital to decomposition, the dominant type depending on climate, litter type and nutrient status. Large active populations of micro-organisms are found in nutrient rich plant litter, with a warm and humid climate, decomposition occurring rapidly. In contrast, small, limited populations are found in acidic, nutrient poor soils, with waterlogged conditions and cold climates.

Decomposition or humification results in the following changes (Hornung and Adamson, 1987):— (i) Loss of organic matter, as a gas, or in solution, as a result of leaching and attack by micro-organisms; (ii) Loss of physical structure; (iii) Change in chemical state, for example, the production of new types of molecules by micro-organisms.

Mineralization is an important part of the decomposition process producing inorganic ions that can be utilized by
plants. In peats, environmental and physical/chemical factors arrest decomposition before the mineralization stage has been reached. If these limiting factors are removed, for example if peat is drained and conditions become aerobic, decomposition is accelerated and mineralization occurs with the production of inorganic compounds such as nitrogen and sulphur, and the release of cations and trace metals.

COMPOSITION AND PROPERTIES
This section covers upland peats only, for further detail see Hornung and Adamson (1987).

The main components of peat are organic material and water. Norwegian peats for example contain between 3% and 10% solid matter by volume, down to a depth of 45cm, at 40cm some 90% by volume is water, Clymo (1983). Inorganic matter (ash) is also low, most peats contain less than 20% of their own dry weight as unburnable inorganic matter. The S.S.E.W. allows up to 60% ash in some of its categories of peat. Water content is high and forms the greatest proportion of weight within the soil, for example, Gorham (1961), found mean water content of 36 peats to equal 1170% of their own dry weight. Inorganic material in peats is commonly dominated by SiO₂, with iron and aluminium hydroxides being important. Such material results from the underlying rocks, usually the Yoredale, Carboniferous Series and the Jurassic Series. Sulphur content is high as
a product of anaerobic decomposition, content increases from the surface into the saturated, anaerobic zone where it remains relatively constant.

The physical nature of water within peat varies. Water in some peats can be squeezed out readily in others it cannot. This depends on the 'form' in which the water is held, i.e., whether it is held by capillary forces or chemical bonds. The form in which it is held varies with the degree of humification. In moderately decomposed peats most of the water is held by capillary forces: in highly humified peats significant amounts of water are held by stronger chemical forces. Von Post described a ten point scale of humification for peat, which has been adapted by Avery and is used by the S.S.E.W., see Table 1.2.

The form in which water is held also affects the movement of water through peats and as such also varies with the degree of humification. In relatively undecomposed peat, water flow follows Darcy's Law quite closely, conductivity is usually $10^{-1}$ to $10^{-3}$ cms$^{-1}$; in decomposed peat conductivity is much lower, $10^{-6}$ cms$^{-1}$.

The dry bulk density of peat is very low, due to its high water content, and low inorganic content. Sphagnum peats generally exhibit densities from $0.05$ g cm$^{3}$, in the top 1 or 2 cm, declining to $0.02$ - $0.04$ with depth, before increasing to $0.1$ - $0.2$ g cm$^{3}$ below about 30cm. Bulk density
increases with the degree of humification \((H)\) on the Von Post Scale, indicating that water holding capacity is closely related to bulk density.

When characterising peats, the fibre content is defined by the proportion of organic matter which fails to pass through a 1.5mm mesh sieve. Fibre content is closely related to the degree of humification and hence, the mechanical and hydraulic properties of peats. Fibre comprises of leaves and stems of \textit{Sphagnum} and other bryophytes, sedge leaves and fragments of woody plants. Most of the true fibre comes from \textit{Eriophorum} in the form of undecomposed shoot bases.

Peat chemistry divides into two basic categories; organic which is affected by the nature of the original plant material; and inorganic, affected by the supply of inorganic solutes from the atmosphere or in waters draining into the peat. Both categories are also affected by the activities of animals, micro-organisms, environmental conditions and the age and history of the peat.

The organic chemistry of peats is studied by treating peat with one or more extractants, then attacking the extracted phase until the component parts remain. Organic constituents separate into a number of groups, eg; waxes, hemicellulose, cellulose, lignin, and humic substances (humic and fulvic acids). Humic substances are that
fraction which is soluble in alkali or neutral sodium pyrophosphate. After acidification of this fraction the material which remains in solution is fulvic acid. The precipitate that remains is commonly treated with ethanol, and the insoluble fraction that remains classed as humic acid. Further details and the range of methods used to characterise humic substances in peat are given in Schnitzer and Khan (1978).

The composition and properties described above are common to the peats present in the research sites, i.e., the Winter Hill Association (WH1011b). Other soils at these sites, Wilcocks Association (Wi72ic), Belmont Association (651a, 311a) and the Maw Association (652) also exhibit these properties but only in their upper organic layers.

DESCRIPTION OF BRITISH UPLAND PEATS
Peats at the research sites are classified as upland peats.

Upland peats are dominated by blanket bogs which although widespread in Britain are not commonly found on a worldwide scale. These peats have formed on extensive bench like areas in western and upland Britain. The benches, which result from the geomorphological history and bedrock geology of these areas are covered in drift and were deposited during the Pleistocene. These deposits are heavily textured, some weather easily and most are naturally acidic; those that were calcareous have become
Table 1.4
AREA OF PEAT SOIL ASSOCIATIONS ON NORTHERN ENGLAND 1:250,000 SOIL MAP (JARVIS ET AL. 1984)

<table>
<thead>
<tr>
<th>Soil association</th>
<th>Map symbol</th>
<th>Area (Km²)</th>
<th>%</th>
</tr>
</thead>
<tbody>
<tr>
<td>Adventurer’s</td>
<td>1024a</td>
<td>45</td>
<td>0.14</td>
</tr>
<tr>
<td>Altcar 1</td>
<td>1022a</td>
<td>26</td>
<td>0.08</td>
</tr>
<tr>
<td>Altcar 2</td>
<td>1022b</td>
<td>&lt;2</td>
<td>&lt;0.01</td>
</tr>
<tr>
<td>Longmoss</td>
<td>1011a</td>
<td>213</td>
<td>0.69</td>
</tr>
<tr>
<td>Turbary Moor</td>
<td>1021</td>
<td>3</td>
<td>0.01</td>
</tr>
<tr>
<td>Winter Hill</td>
<td>1011b</td>
<td>2164</td>
<td>7.00</td>
</tr>
<tr>
<td><strong>Total</strong></td>
<td></td>
<td><strong>2451</strong></td>
<td><strong>7.92</strong></td>
</tr>
</tbody>
</table>
acidified in post glacial times by the leaching of their base cations. This has resulted in the formation of poorly drained acid soils which, in the cold wet climate of the uplands, became dominated by vegetation which is tolerant to these conditions.

Decomposition in these soils proceeds slowly due to the climate and the nature of the vegetation, the climate is cool, with high rainfall (greater than 1500mm/annum and/or 200 rain days) and the vegetation is acidic. Soils are also waterlogged due to heavy rainfall and the level, or gently sloping, terrain. Such conditions lead to a build up of organic matter and the peats formed in this way, are classed as climatic peats. Other workers (Smith and Taylor, 1969) have identified anthropogenic peats which formed in areas of the uplands that carried woodland in post glacial times. Clearance of these woodlands by man lead to increased soil wetness, rapid leaching and acidification, forming a habitat only suitable for plants which tolerate acid waterlogged conditions.

Upland peats are dominated by two Soil Associations, the Longmoss and Winter Hill, these are described as 'raw oligo-fibrous peat soils'. Table 1.4 the Winter Hill Association forms the most extensive coverage of peat dominated soil in northern England, covering 7% of the area. A further 10% of the area is covered by soils with
peaty surface horizons (too thin to be mapped as peats), which may influence water quality in terms of the organic matter they contain.

**COMMENTS ON THE STABILITY OF PEAT DEPOSITS**

Peat deposits are inherently unstable due to their unconsolidated nature and once exposed, they erode rapidly. Most of the peat areas in upland Britain are currently eroding, only a relatively small area is still actively growing.

Erosion can be divided into two main groups, that caused by the physical elements and that caused or initiated by man.

'Natural' erosion occurs as a function of the structure of peat and the climate of the uplands. Water and wind erosion are common, flowing water produces channels that can eventually merge, leaving isolated islands of peat known as hags, these are then exposed to wind erosion. Mass movement in the form of peat slides also occur, due to the accumulating layers of peat becoming unstable.

Erosion attributable to man's activities is initiated in several ways and is becoming increasingly important. Greater access to the countryside has caused recreational pressures which lead to trampling and accidental fires. Atmospheric pollution has lead to a change in the botanical
composition of plant communities, *Sphagnum* has become noticeably less common leading to a reduction in the moisture holding capacity of vegetation. Overgrazing and heather burning for grouse management have also created problems. All of these factors potentially expose peat in turn, to a greater amounts of 'natural' erosion.

Although there is no evidence to suggest that there has been dramatic increase in the extent of erosion over the last 60 years. Taylor (1983) recognised that isolated peat hags at high altitudes in the Pennines were unlikely to have been influenced by man. However, man's influence is apparent in specific locations where large increases in erosion have occurred, for example, along the Pennine Way and the Lyke Wake Walk.

Control of erosion is difficult and once peat has become unstable, it is even more difficult to re-establish as natural revegetation is inhibited because of the surface instability and low nutrient supply. However, research has demonstrated that it is possible to reintroduce vegetation and reverse and control erosion.
AIMS AND OBJECTIVES, RATIONAL, ANALYTICAL AND EXPERIMENTAL METHODS.

2.0 AIMS AND OBJECTIVES

This research is designed to investigate the temporal and spatial variation in raw water colour at a catchment and identify any anthropogenic catchment characteristics that, through catchment management or modification, result in raw water discoloration. Earlier research results have shown that moorland burning and ditching may have a significant effect on the production of soluble colour in supply. Consequently, detailed objectives have been considered for these factors of moorland management.

For burning; to assess whether moorland burning increases the production of colour over that produced by unburned moorland and whether such increases differ in magnitude, depending on the fire characteristics of the burn.

For ditching; observations have been made of the variations in colour between individual ditches within catchments; fluctuations in colour levels have been considered in line with fluctuations in the water table and the influence of drainage on soil moisture levels in terms of, the potential impact of drainage, on colour production.
A further type of catchment management has also been addressed, in response to suggestions from the Yorkshire Water Authority, that liming may reduce the levels of soluble colour in supply. This hypothesis has been investigated with a view to answering the following objectives; to assess whether moorland liming will increase or decrease soluble colour in supply, and to assess whether increases/decreases differ in magnitude depending on the quantities of lime applied.

For burning, liming and ditching the potential processes resulting in the increase or decrease of colour production have been considered to allow the formulation of simple management strategies, designed to reduce colour in supply.

Finally, as colour is thought to be associated with aluminium, iron and manganese levels in water supplies, these ions and their relationship to colour has been considered throughout this research.
The considerations on the previous page are incorporated in the following broader aims:

(a) To investigate the Water Catchment Management and Modifications (anthropogenic) which lead to raw water discoloration and gain an understanding of the processes involved.

(b) To explain the spatial and temporal variations in raw water colour, due to these processes.

(c) To identify catchment types subject to the most risk, and to determine which particular Water Catchment Management/Modification techniques cause them.

(d) To produce simple management strategies to reduce/control discoloration at source.

2.1. REASONS FOR RESEARCH

2.1.0. CONCERNS OF WATER COMPANIES ABOUT RAW WATER QUALITY IN TERMS OF COLOUR AND DISSOLVED METALS

As previously mentioned, only some Water Companies are adversely affected and therefore more concerned with the problems of water treatment, domestic and industrial consumer complaints, and in meeting EC standards. Those
currently unaffected may suffer future problems as either environmental pressures increase or climatic change occurs, or both. Changes in water quality affect the policies of companies in terms of catchment management and the need for new water treatment works.

2.1.1. INCREASING COSTS OF WATER TREATMENT

A number of Water Company treatment works have only single stage treatment, usually some form of filtration often preceded by limited chemical treatment. Many of these works are supplied from Pennine catchments and therefore can be adversely affected by deterioration in raw water quality. At a number of works once raw water quality has deteriorated beyond a certain point the treated water quality also deteriorates. An extreme example of this problem is found at sand filtration works, where the treated water quality is at the mercy of the raw water quality. Such works produce a water, whose quality shows a similar seasonal trend to that of raw water, albeit at a lower level. During the Autumn of 1985 this effect showed itself at certain treatment works where the final treated water colour exhibited the same rapid increase in colour as observed in the raw waters. Although this effect can be identified almost every year, the magnitude of the deterioration was much worse than in previous years.
At works where there are two or more stages of treatment there is far more scope for the adjustment of the process control parameters and the effects of deterioration in raw water colour, are more easily dealt with. For example, at Chellow Heights (Bradford), the quality of the treated water has been largely maintained despite dramatic fluctuations in raw water quality, which showed significant deterioration during the Autumn of 1985 and the colour of the treated water has been largely kept below 1.5 Abm⁻¹.

Whilst a modern, well designed, multistage treatment works can be operated to treat severely discoloured raw waters there is a financial penalty. Colour is removed primarily by the use of aluminium sulphate coagulant, as colour increases so does the amount of coagulant required. At Chellow Heights the amount has increased considerably and it is estimated that during Autumn 1985 an extra £57,000 was spent on treatment chemicals for this works alone. Other significant cost increases include for extra filter backwashing and sludge disposal and the material cost of coagulant at Ramsden Wood has increased three-fold since 1979, see figure 1.3. Additional capital spending is also incurred in building multistage treatment works. River abstraction does not present a long term viable alternative as it incurs 5-10 times the cost of upland supply.

All costs have to be met by the Water Companies and in turn, by their customers, particularly in the climate of
complete profit viability occurring since privatisation. It is notable that the cost and cost increases mentioned and above are significantly historic and have already been exceeded by current levels and will go on rising. Personal communication from J. Warne, Yorkshire Water, indicates, for example, that the treatment process formerly employed at Thrum Hall Treatment Works, which previously received water from Ramsden Wood and closed in 1987, is obsolete to the extent that current treatment processes are much more complex and include not only coagulation but the additional processes of dissolved air flotation, filtration and disinfection.

2.1.2. INCREASING DOMESTIC/INDUSTRIAL CONSUMER COMPLAINTS

Colour in water is something that most people would like to eliminate. On aesthetic grounds alone, highly coloured water is undesirable for domestic and industrial use. Visual impact is not the only objection, it has been claimed that humic acids cause taste in water.

Certain industries are particular about the colour of the water that they use because of the possible effects on their product, e.g. Food Processing, Brewing, Textiles, Pulp and Paper.

Consumer complaints regarding discoloured water show a similar seasonal trend with complaints rising rapidly in
the Autumn. The long term trend in complaints is relatively constant (once the seasonal variation has been excluded) up to the end of 1984. Whilst the number of complaints rose dramatically in Autumn 1985 the figures should be treated with caution, owing to the quality shortfall temporarily caused by renewal of process plant and distribution systems. Nevertheless it is clear that the problem of raw water discoloration affects not only the Water Companies performance, in water quality terms, but also the public’s perception of that performance.

2.1.3. TREATED WATER QUALITY WITH RESPECT TO EC LIMITS

There is no evidence that the materials which cause discoloured water are directly injurious to health. It is possible however, through solubilisation of metals such as aluminium from peat and coagulant, that consumption of coloured water over a long period could be dangerous as aluminium has been linked with Alzheimer’s Disease. Solubilisation of lead caused by increased acidity may also present problems over extended periods.

It has been claimed that humic acids interfere with chlorination, and that they may encourage bacterial growth in the water, presumably by acting as a nutrient. Suggestions have also been made that organics in the form of humic substances are the precursors to potentially carcinogenic Trihalomethanes.
For these reasons and those of aesthetic quality EC standards are formulated and Water Companies must try to meet them. The key standards relating to discoloured water are:

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Limit</th>
</tr>
</thead>
<tbody>
<tr>
<td>Colour</td>
<td>1.5 Abm(^{-1})</td>
</tr>
<tr>
<td>Aluminium</td>
<td>0.2 mg/l</td>
</tr>
<tr>
<td>Iron</td>
<td>0.2 mg/l</td>
</tr>
<tr>
<td>Manganese</td>
<td>0.05 mg/l</td>
</tr>
<tr>
<td>pH</td>
<td>&gt;5.5 &lt;9.5</td>
</tr>
</tbody>
</table>

Exceeding such limits now results in the potential imposition of fines on Water Companies by the EC Directive, another extra cost that may be passed on to the consumer.

2.1.4. **INVESTIGATION/PRODUCTION OF SIMPLE MANAGEMENT STRATEGIES**

An alternative to building new treatment works is to produce simple strategies to combat discoloration at source. Anthropogenic factors which increase colour levels may be controllable by better moorland management and simple engineering, to exclude the most coloured waters from the raw supply. Natural effects are much less controllable, in view of their scale and potential link to global warming and the only method of control may be to exclude the worst affected catchments from supply. Such management alternatives may be less costly than a programme
of new treatment works. For example, Yorkshire Water by 1995 will have invested £85M in replacing old treatment works.

Cost apart however, good management of moorland is the only way of protecting water resources at source and as such should be encouraged in line with the programme of new treatment works.

2.2. RATIONALE BEHIND THE RESEARCH.

As discussed in Section 1.0.2. Edwards (1987) has identified several potential causes to explain increases in water discoloration, these divide into natural and anthropogenic factors. This research deals with two of the anthropogenic factors identified, namely burning and ditching. The third area liming is addressed in response to the suggestion that increased colour levels may be a result of acidification and in response to this that large scale terrestrial liming may reduce colour.

Research began with large scale catchment studies the reasons for which are outlined below.

As indicated in Section 1.0.1. large variations in colour levels occur between different catchments, an effect currently apparent in Wales, Scotland and especially Yorkshire.
Within the Pennines, catchment areas exhibit quite marked differences in their geomorphology, vegetation and land use, which may explain the variation in colour values.

Just as there is variation between catchments, it is not unreasonable to look for differences within subcatchments which are often inherently different in terms of their size, soil association, and geology. In addition there may be variations in the management practices used by landowners. Consequently, apparently similar subcatchments may be subjected to burning at different frequencies, with greater or lesser care; they may be limed at differing doses; they may be drained or redrained to different intensities and by different techniques; and they may be subject to different grazing pressures.

These differences may seem inconsequential when compared to physical catchments differences but since uplands exhibit such fragile ecosystems they may be of comparable importance and their causes are also more likely to be identified on a subcatchment scale, where they can be isolated.

Work involved the measurement of catchment characteristics, consideration being given to catchment size, pedology particularly the area of peat within catchment, and the effects of moorland management, ditching and burning.
These characteristics were then related to water quality in terms of colour and levels of metals.

This work revealed that burned and ditched catchments produced greater quantities of colour than catchments where these practises were absent.

In response to this more detailed studies were undertaken to confirm that these management practises did increase colour production, consideration was also given to the processes involved.

Burning experiments began on a small scale and were carried out solely to discover whether or not there was a difference in the levels of colour and metal ions produced by peat from burnt and non-burnt patches of moorland.

These experiments confirmed that burning influenced colour, and in response large scale studies were carried out. These involved the sampling of cores from patches of burned and non-burned moorland over a period of one year to assess the effects of burning. Two areas were used one representing a low temperature burn and one representing a high temperature burn. The response in terms of colour, between different temperature burns was seen to be important in identifying the processes involved in colour production and the formulation of management strategies. The importance of temperature was further investigated by
the laboratory burning of cores at differing temperatures. The effects of severe burning compared to those of managed burns were also addressed in a short catchment study, to see if the relative effects of fire differed in their response to colour production thereby identifying processes and the relative importance of "good" heather management. The effects of burning on soil moisture were considered as reduction of soil moisture creating aerobic conditions appears to be instrumental in colour production. Soil moisture studies included changes in microclimate, core measurements and measurements over time in an experimental block which had been burnt.

The effects of ditching were further addressed by extensive sampling of ditches within catchments identifying the spatial and temporal variations in colour. The effect on water table fluctuations and the resultant colour were also considered via the tube well studies. Effects on soil moisture were measured over time to demonstrate the effect of ditching on soil moisture levels compared with undrained peat.

Studies on liming were undertaken because it has been suggested that extent of liming may have a correlation with the presence and level of colour there being a belief that the decline nationally (by half in the 1960's), has led to an increase in colour. Some Water Companies, e.g. Yorkshire Water, propose that massive doses of lime will reduce
colour whilst others suggest that liming will increase its presence. Detailed work on liming has therefore been undertaken. (Some attention is also paid to the effects of grazing and atmospheric pollution.)

Initial studies were small scale, peat being shaken with differing doses of lime, to assess the effect on colour and identify the dose at which colour was reduced or increased. Liming was found to have an effect on colour generation and consequently large scale experiments were undertaken, namely the liming of soil cores at differing doses. Cores were leached and certain parameters measured to assess potential processes. Large scale studies were also undertaken in the field, massive dosage being applied to a block of peat, to assess the proposed management of colour by liming.

Specific relationships between levels of soil moisture and colour were not considered as these formed the basis of work undertaken by Mitchell (1990), discussed below.

ASSOCIATED WORK WITH WATER DISCOLORATION, THE "NATURAL" PROCESSES OF COLOUR PRODUCTION

Research into the natural processes has been carried out by Dr. G Mitchell, School of Geography, University of Leeds. Such work is complementary to that of anthropogenic processes and as such should be considered.
OTHER COMPLEMENTARY WORK

Prof A McDonald  School of Geography, University of Leeds.
Dr P Naden  Institute of Hydrology.
Dr E Tipping  Institute of Freshwater Biology.
Mr R Norton  Water Research Council.
Prof D Kay  St David’s University College, Lampeter.

2.3. RESEARCH SITES.

2.3.0. LIST OF SITES

i) Howstean and Inmoor valleys, situated adjacent to Scar House and Angram reservoirs. Upper Nidderdale, North Yorkshire.

ii) Thruscross and Fewston reservoirs. Upper Washburn Valley, North Yorkshire.

iii) Glaisdale Moor, Near Rosedale, North Yorkshire Moors.

iv) Gunnerside Moor, Gunnerside, Upper Swaledale.
2.3.1. REQUIREMENTS OF SITES, REASONS FOR CHOICE AND ASPECTS OF RESEARCH USE.

HOWSTEAN AND INMOOR CATCHMENTS, UPPER NIDDERDALE

This site was the most widely used, and covered many aspects of the research. Primarily it was chosen for its suitability for a large scale catchment study of the spatial variance of discoloured water, leading later to smaller scale studies on the effect of liming, burning and ditching on colour generation including field experiments and removal of peat cores for laboratory experiments.

The initial requirements of the site were a large number of small sub-catchments within a reasonable distance, that could be sampled on a regular basis, exhibiting a different range of land uses and agricultural practises/management.

The site has 28 subcatchments in all, 1-15 situated in the Howstean valley, 16-28 situated on Inmoor. Physical differences in the area are kept to a minimised by the choice of a single large catchment where rainfall and geology are potentially similar. Rainfall rises to an annual average maximum of 1500mm and the geology is comprised of the Carboniferous Millstone Grit Series d4 composed of sandstone and shale. Pedology comprises the Winter Hill series (1011b), Wilcocks series (72ic),
Belmont series (Belmont 651a, Revidge 311a) and the Rivington series (541g).

Such similar physical characteristics, enabled comparisons to be made between similar sub-catchment types with different land use and management strategies, thereby highlighting any anthropogenic effects on water discoloration.

Further, the catchment and its surrounding area generates some of the highest levels of discoloration within the Yorkshire region, measured at Chellow Heights treatment works, Bradford, which receives water from Scar House and Angram reservoirs fed, in part, by the Howstean and Inmoor valley. Thus any differences in catchments regarding colour and land use should be easier to demonstrate and to establish the factors involved.

FEWSTON AND THRUSCROSS RESERVOIRS, WASHBURN VALLEY
Research in this area was limited to a large scale catchment study, similar to that of Howstean and Inmoor. The requirements were the same, for a number of small catchments exhibiting similar physical characteristics with differing land uses and management practises. The work was undertaken primarily to contrast with the above study although lower colour values were expected as those measured at Headingley Treatment Works, Leeds, are generally lower. Geology and soils are the same as
Howstean and Inmoor with the addition of the Dunkeswick (711p) and Maw (652) Soil series. Conveniently also, the site is passed on the way to Nidderdale.

GLAISDALE MOOR, NORTH YORKSHIRE MOORS
Research here consisted of a study of sub-catchments that were severely burnt in a heath fire in 1976. The aim was to compare the effects of accidental severe fires with controlled management burns at Howstean. Requirements were the same as those at Howstean, a number of small catchments within a large catchment, exhibiting similar physical characteristics.

The site was similar to Howstean in terms of physical characteristics, geology - dominated by sandstones, shales and clays, Middle Jurassic Deltaic Series, (formerly known as the Esturaine Series), pedology - primarily Winter Hill series (1011b) and high rainfall.

GUNNERSIDE MOOR, SWALEDALE
Research here was designed to complement work on ditching done at Howstean. The area had recently been ditched and comprised similar physical characteristics to Howstean, although the precise peat formation was slightly different, being a blanket peat rather than a bench peat.
2.3.2. DETAILED DESCRIPTIONS OF PHYSICAL CHARACTERISTICS

TOPOGRAPHY
All of the above sites have similar topography, equating to Moorland catchments. Relief is above 305m and rainfall high, >1500mm. Vegetation and soils are similar and have been influenced by man, creating an impoverished and exposed habitat.

GEOLOGY
Excepting Glaisdale, all the sites consist of the Yoredale series, a facies of the Lower Carboniferous in Britain. Such geology is common in upland areas of the Pennines, the rocks form a cyclic sequence in which marine limestone is succeeded upwards by marine shales, shales and silty shales, current-bedded sandstones and finally, thin coal. The Glaisdale site (NYM) is of the Lower and Middle Jurassic Series; consisting of lias (largely mudstone), Cleveland iron stone, Staithes formations and moor grit (part of the Ravenscar group - non marine siltstones and sandstones with marine intercalations). Such geology is impoverished in nutrients, acidic (except in limestone beds) and rich in iron and aluminium.

VEGETATION
This consists of acid tolerant plants amongst which the most prevalent are Sphagnum moss, cotton grass (Eriophorum vaginatum), purple moor grass (Molinia caerulea), sedges
(Carex sp.) and Ericaceas dwarf shrubs for example; heather (Calluna vulgaris) and bilberry (Vacinium myrtillus).

The combination of the plants in the community is affected by the type of land management, the impact of pollution and the development stage of the bog. In large areas of the Central Pennines atmospheric pollution has severely limited Sphagnum and cotton grass has become the dominant vegetation. In some areas Molinia has spread as a result of overgrazing and burning, whilst in others, similar management has produced Calluna dominated vegetation. Natural changes occur as the peat deposits thicken and become relatively drier, Calluna and acid tolerant grasses becoming dominant.

Vegetation at the research sites largely complies with the above description, dominant species being a product of management. Howstean and Inmoor consist largely of moorland, the drier parts of which are dominated by Calluna vulgaris, managed by burning whilst the wetter areas consists mainly of acid tolerant grasses such as Molinia and Eriophorum. Areas of permanent pasture exist on the fringes of the moor.

The Washburn site is lower and is comprised mainly of permanent pasture and coniferous plantations. The higher streams in the head of the valley run on to moorland where
**Calluna vulgaris** is dominant as a result of management by burning.

Gunnerside, which used to be dominated by **Calluna** is now mainly acid tolerant grassland, consisting of **Molinia** and **Eriophorum**, possibly as a result of overgrazing.

Glaisdale, before 1976, was dominated by **Calluna** and managed as a grouse moor, but after a severe fire in 1976, the vegetation was largely destroyed. Today, some 14 years later, patches of the moor still remain bare and others are still colonized by the primary succession i.e., mosses, algae and lichens, although some areas now support young heather plants. On the edges of the fire zone **Calluna** dominates and bilberry (**Vacinium myrtillus**) is fairly common.

**CATCHMENT AGRICULTURE**

Agricultural activity is the same at all sites, namely hill sheep farming and at Howsteans and Inmoor, cattle are also supported on the permanent pasture. Moorland areas at the sites are managed as Grouse Moors and parts of the Washburn support coniferous plantations.

**CATCHMENT RECREATION**

All sites are open to the public, accessed mainly by footpaths across the moors and grouse shooting takes place in all catchments.
2.3.3. DESCRIPTION OF RESERVOIR DESIGN. INCORPORATING HOWSTEAN AND INMOOR, NIDDERDALE

Howstean and Inmoor are situated in a valley adjacent to Scar House and Angram reservoirs. Each of the sub-catchments in the valley has an intake which channels water into an aqueduct; the water then flows into the Scar House valley and into the reservoir. Intake flows can be excluded from the system by 'turning out' i.e., opening the sluice gates and allowing the waters to flow down their natural stream beds. See Figure 2.1.

2.4. EXPERIMENTAL DESIGN AND DESCRIPTION.

2.4.0. LARGE SCALE CATCHMENT STUDIES.

CATCHMENT SIZE

This was assessed so that the percentage area of deep peat i.e. the Winter Hill Series (1011b) could be calculated for each of 28 catchments at Howstean and Inmoor. Two information sources were used, aerial photographs (scale 1:27 000) and Ordnance Survey Maps (scale 1:10 000). Catchment divides were placed by observing contours and stream networks on both sources and aerial photographs were especially useful as they gave stereoscopic views and provided a good visual concept of terrain. Much more detail of the drainage networks of each subcatchment were apparent.
Fig. 21 Upper Nidd catchments showing How Stean and In Moor intake systems.
on the photographs than were indicated on the maps; low order streams being clearly visible. The photographs also indicated the drainage ditches; these also had to be considered, as some of them captured waters from other catchments, increasing their subcatchment areas.

AREAS OF DEEP PEAT
These were charted by using a 1:25,000 soil map of the area provided by the Soil Survey of England and Wales (unpublished). Areas of different soil types were plotted on to 1:10,000 map of the catchments and expressed as a percentage for each subcatchment by point counting techniques. A 1:50,000 geological map was also considered.

LENGTH OF DRAINAGE DITCHES WITHIN SUBCATCHMENTS.
These were measured, from the aerial photographs for Howsteaean and the 1:10 000 map for Inmoor, using an opisometer. Length of ditch (moorland gripping) and drain (water authority drainage) are expressed per unit area of the subcatchment. Moorland gripping has two phases, first at Howsteaean when subcatchments 6-12 and 14, were ditched in 1974 and again in 1984 when subcatchments 13 and 15 were ditched, but as this was later than the aerial photography, their lengths could not be measured, however the ditching density is known to be higher than in 1974.
PRESENCE OR ABSENCE OF HEATHER BURNING.
Information was supplied by Mr J.H.Ramsden, Head Gamekeeper, Howstean but area was not measured owing to the complex pattern of irregular, multi-aged burns. Subcatchments H/S 2 and I/M 1 are the most regularly and intensively burnt.

VEGETATION AND LAND USE.
Although observed, these were not measured as to all intents and purposes they mirror changes in pedology or the presence of burning.

POINT COUNTING TECHNIQUE
This involves the measurement of areas on maps by using a 'dot planimeter' which is a transparency printed with a dot matrix, each dot representing a unit cell measuring 4x4mm. and equivalent to an actual area of 0.0016km², Stellingwerf (1966) and Frolov and Mailing (1971).

SAMPLING SITES FOR COLOUR AND CATCHMENT CHARACTERISTICS.
Howstean and Inmoor catchments were sampled just above the intakes of each stream before the waters entered the aqueduct at positions which can be seen on Fig. 2.2 and Fig. 2.3. Periodic sampling occurred between 24.2.1986 and 2.3.1987 at Howstean and between 18.7.1986 and 30.5.1987 at Inmoor.
Howestan Catchments Pedology

Fig 22

SOIL SERIES KEY

- Winter Hill (Y8/Y6)
- Revidge & Belmont (r10/r9)
- S7
- Winter Hill (Y11)
- Wilcocks Series (Wi)

--- Boundaries of catchments

1. No name
2. Armathwaite Gill
3. Armathwaite Butts
4. Blackawell Lathe
5. Buskar
6. Crake
7. Aygill
8. Dunlin
9. Egret
10. Fieldfare
11. Staining Gill Beck
12. Great Blowing Gill Beck
13. Straight Stean Beck
14. Backstean Gill
15. Little Backstean Gill
16.
Washburn sites were sampled directly from the stream at the locations mapped on Fig. 2.4. Sites 4-9 represent more intensive spacial sampling to try and assess the effects of clear felling.

Samples were taken in polythene bottles that did not absorb colour or metal ions. An autosampler was also set up at the Scar House end of the aqueduct, which sampled the collective waters from Inmoor and Howstean.

2.4.1. BURNING EXPERIMENTS.

SMALL SCALE LEACHING AND SHAKING EXPERIMENTS (LABORATORY).
Peat was collected from areas of Howstean and Inmoor in the form of cores and then divided into sections 5cm. thick; 25g. were taken from each section and placed in leaching tubes and leached with 50ml. of distilled water. Some of these samples were each further leached with 50ml. of distilled water per day on a continuous basis for a period of three weeks. Shaking experiments were also conducted using 50g. of peat and 100ml. of distilled water (pH 5.2). Both the shaken and leached samples were then measured for colour, Fe., Al. and Mn.

LARGE SCALE LEACHING OF BURNED AND NON-BURNED CORES.
In March 1988, limited burning took place on the Howstean 2 (stream 1) and the Inmoor 3 (stream 18) catchments. The fire at Howstean was a high temperature fire, flames
reaching several feet high, clearing the area almost entirely of vegetation. Old heather stems were removed completely and the litter partially burnt off, leaving a thin crust. Only in areas where rills had formed wetter areas did mosses and sedges survive. Revegetation was reliant on the seed bank alone as any nodules for vegetative growth had been removed. For the first year the area remained bare, young heather plants appearing in the second year, but only affording sparse cover. Large patches of bare ground still remained in the summer of 1990.

The Inmoor fire, by contrast, was a low temperature burn, small flames progressing slowly, leaving an almost complete vegetation cover. Charred stems of the heather remained together with a ground cover of grasses, mosses and sedges. Regeneration of heather was again slow but the peat surface was protected by the remaining vegetation. Information of fire characteristics provided by Mr S. Cannon, Head Game Keeper, Howstean.

The above sites and adjacent sites which had not been burnt, were sampled on four occasions, April 1988, August 1988, January 1989 and April 1989. On each occasion twelve cores were taken, three each from the high temperature burn at Howstean (referred to as BHS); from an adjacent non-burnt area, (NBHS); from the low temperature burn at Inmoor, (BIM) and from an adjacent non-burnt area, (NBIM).
Soils at the above sites are mapped under different associations HS being the Belmont and IM being the Wilcocks. Although this may initially be seen as a problem when comparing cores, it is evident from the soil descriptions, that the peat layers of these two associations are essentially the same, making comparisons viable. (Two burnt sites of different temperatures and the same soil association, not being available).

Analysis varied between core sets, variables being added to later core sets as work progressed. All variables measured were in response to either postulated relationships, (for example Fe and colour) or to investigate the effects of burning (discussed in Section 1.1.) and their potential effect on colour generation.

Variables included:

For water - colour, Fe, Al, Mn (using A.A.S), pH (by meter), conductivity (by conductivity bridge), anions: NO$_3$, PO$_4$ and SO$_4$ (using liquid chromatography).

For peat - soil moisture (dried at 105°C until constant weight measured) and organic matter (loss on ignition at 450°C)
SOIL CORE COLLECTION.

Soil cores 30cm. deep, were taken using iron formers and were 2.5cm or 5.0cm. wider than the sample pots used in the leaching apparatus. Cores were extracted using a hub-puller to minimize compression of the peat and extraction was done in the field to reduce the time the peat remained in the iron core. The edges of the cores were removed in the laboratory to avoid incorporation of any foreign iron. Soil structure was undisturbed, sections of peat core being directly transferred into the leaching pots which were filled layer by layer as the experiments progressed, minimizing drying out of the lower layers, these layers being kept in sealed polythene.

RAINFALL CHEMISTRY

The rainfall at four sites around the Nidderdale field site was monitored weekly for a period of one year and pH, Cl\(^-\), SO\(_4\), PO\(_4\) and NO\(_3\) were measured. Anions were measured using liquid chromatography. The results of analysis are given in Appendix A and were used to produce the simulated rain used in all the leaching experiments. The chemistry of this rain represented the mean of natural rain observed in Nidderdale, its composition being based on the mean of pH3.89: anions equalling; 9.8ppm. chloride, 7.00ppm. sulphate, 1.14ppm. phosphate and 2.88ppm. nitrate. Final
pH was adjusted using acetic acid or sodium hydroxide, so as not to introduce further, those ions mentioned above.

RAINFALL SIMULATION

Cores were leached with 'chemical' rain from two small rainfall simulators each having thirty hypodermic syringes tipped with 0.8mm. (internal) needles and covering six cores. The simulators were placed above the cores on a moving platform so that droplets fell randomly on their surfaces, avoiding selective wetting and repeated impact from droplets. The amount of rainfall was approximately 4mm/hr⁻¹, in order to obtain a sufficient sample from successive layers on successive days, due to the low hydraulic conductivity of peat. This minimized the length of time the cores were exposed to laboratory conditions, potential laboratory effects being reduced by using an unheated, dark laboratory.

LEACHING APPARATUS.

The leaching system consisted of twelve stacks each one having five tiers of pots, each pot contained a slice of the field cores. The top tier held the litter from each core, those below each held 5cm. sections, down to a depth of 25cm., each section was contained in a 10cm. dia., plastic 'pot'. The tiers were so constructed and sealed as to ensure that only simulated rain and leachate drained from each sample to the one below and that water which had drained either down the outside of the pot or between the
inside of the pot and the sample were excluded. Therefore any "edge effect" was avoided. In addition, samples were taken between each tier in order to measure and compare the flow from layer to layer and to provide a more realistic pattern of colour flows, with depth, as the soil water had flowed down through each tier, picking up colour, metal ions and anions as it progressed. In this way field conditions were duplicated.

Two leaching racks were used, each rack holding six cores, each placed beneath rainfall simulators enabling twelve cores to be leached simultaneously.

This apparatus is shown in appendix A.

EXPERIMENTAL METHODS OF CORE BURNING (LABORATORY).

The design of this experiment was identical to that described in Section 2.4.1.

The method involved the collection of twelve non-burned cores from Howstean 2 (stream 1), of the Belmont Soil Series. Three were left non-burned. The top surfaces of each of the others were then burnt in the laboratory; for between 1.5 and 2 minutes, three each at 300°C, 600°C and 800°C. Burning was performed with a 'garden' flame thrower allowing the required flame temperature to be obtained before burning started, the sides of the cores were protected by metal sleeves during burning. Temperatures and
duration of burn matched those of normal management burns, see 4.0.2.

After burning the cores were removed from their metal sleeves and sampled for soil moisture at the surface and at depths of 1, 2, 4, 6, 8, 12, 16 and 20 cms. They were then wrapped in polythene, (left open at the top), put out in the open for a month and sheltered from rainfall. Afterwards they were sectioned and leached in the laboratory and soil pH (using 0.01m CaCl$_2$); organic matter and soil moisture (after leaching), were measured. Resulting leachates were analyzed for pH, Fe, Al, Mn, NO$_3$, PO$_4$, SO$_4$, and conductivity. (Fe and Mn measured by A.A.S; Al measured by I.C.P. and anions measured by liquid chromatography.) In addition, small samples (21.9g) were taken from each core section and shaken with 100mls of 'chemical rain' for 24 hours, as it was thought that agitating the peat may enable it to rewet more quickly. This was done in the anticipation that the burned cores would be difficult to rewet, a factor common to peats when they lose water.

MICROCLIMATE STUDIES

This small scale study was undertaken in response to the work of other authors, discussed in Section 1.1.2., and as a result of the apparent lack of permanent differences in soil moisture between burnt and non-burnt cores as discussed in Section 4.0.1. Results from leached cores
indicated that normal management burning does not alter the chemical properties of peat sufficiently to alter gross measurements of soil water. It seems probable therefore that the differences between burnt and non-burnt soil moisture recorded by Anderson (1980) Bridges (1986) and Birch (1958a) and inferred by various authors, notably Mallik, Gimingham and Rahman (1984) from the lowering of infiltration capacities; are linked to changes in microclimate rather than chemical alterations, in the case of 'normal' management burns.

Measurements of the basic variables which affect microclimate were taken on three occasions over the summer of 1989 for the same burnt and non-burnt patches as those from which field cores were taken. Soil temperature measurements were also taken for blocks 1 and 3, (the nature and purpose of these blocks are discussed in Section 2.4.3.), Block 1 was an untreated control block and Block 3 was been burnt.

**SMALL SCALE STUDY OF THE SEVERE FIRE AT GLAISDALE**

This study was undertaken to look at the effects of severe fire on colour generation. Glaisdale, on the North Yorkshire Moors having experienced an accidental moorland fire in the summer drought of 1976. A number of subcatchments were sampled, some having been subjected to management burns and others to the severe fire of 1976.
2.4.2. LIMING EXPERIMENTS.

SMALL SCALE SHAKING EXPERIMENTS ON PEAT LIMED AT DIFFERING DOSES.

Two large peat samples were taken from the Howsteanean area, one from poorly humified, deep peat (Winter Hill Series), the other from a relatively well humified shallow peat deposit (Winter Hill/Wilcocks Series). Organic matter content for the two soils was similar, at 96.6% and 84.7% respectively. Forty two sub-samples, each equal to an area of 8 cm² were separated and divided into six groups of seven sub-samples. One sub-sample from each group was left unlimed, the remaining six were limed at an equivalent of 1, 2, 4, 6, 8 and 10 tonnes/ha. Three groups were shaken for twelve hours, one with 100 ml of distilled water (pH 5.8) and the other three groups were shaken with 100 ml of chemical rain (pH 3.8). The resulting samples were filtered, coloured and measured for pH.

LARGE SCALE LEACHING EXPERIMENT OF CORES LIMED AT DIFFERING DOSES.

Twelve cores were taken from a un-burned site at HS2 (stream 1) by the method already described. Three of these were left unlimed and of the remainder, three each were limed equivalent to a dose of 0.31, 0.93, and 1.5 tonnes per hectare.
Following liming all the cores were exposed to chemical rain by rainfall simulation, until flow was detected from the base of the core. Cores were then wrapped in polythene, left for one month, sectioned in the usual manner and then leached again, using simulated chemical rain pH 3.8.

Note. Originally, the doses were planned to equate to 2, 6 and 10 tonnes per hectare but unfortunately, owing to an error in calculation, the actual doses applied were equivalent to 0.31, 0.93, 1.5 tonnes per hectare. Although the planned doses would probably have produced more indicative results some useful comments do emerge. Ideally this experiment should be repeated at the planned dosage.

2.4.3. LARGE SCALE FIELD EXPERIMENTS, BURNING, LIMING AND DITCHING.

METHOD - CONSTRUCTION OF BLOCKS.

Four experimental blocks were isolated from the Winter Hill peat upon Inmoor, Nidderdale, in order to observe the effects of drainage and differing treatments, one to act as a control, one to represent burning, one to simulate drought conditions and one to be limed. The single ditched face of the moor, exposed by the isolation of the blocks offered a moor-edge surface for control purposes. Each block was approximately 1.5m square and 0.5m high. Four layers of damp proof membrane were inserted into the front
faces of these blocks, the first being close to the surface of the block the others being spaced at approximately 20cm intervals. Sampling of throughflow from these layers began in October 1987 for a calibration period lasting until the end of March 1988, when the blocks were treated.

Block 1 (B1) remained untouched and uncovered, as a control.
Block 2 (B2) was completely covered by a tarpaulin to simulate drought.
Block 3 (B3) was burnt, conditions being representative of a 'severe burn'. Temperatures in the order of 900°C were achieved and maintained for 30 minutes, surface litter was partially burnt but little heat was actually transferred to the subsurface layers, temperatures at 1cm below the surface remaining below 100°C.
Block 4 (B4) was limed equivalent to a massive dosage of 17t/ha.

The throughflow was sampled on a weekly basis whenever possible and measured for colour, pH, Fe, Al, and Mn.

Block 2 (droughted) and the face of the moor (moor edge control), exposed from where the blocks had been cut, were also sampled for throughflow. These results are discussed by Mitchell (1990). Photographs of these blocks, pre and post treatment, are reproduced in Appendix A.
EFFECTS OF DRAINAGE ON SOIL MOISTURE.

Soil Moisture was measured for each block, including the single ditched face of the moor, and for an area of moor unaffected by ditching (control). Soil moisture was measured at the surface and then at 10cm intervals to a depth of 1m, using a Institute of Hydrology Neutron Probe. A calibration curve for soil moisture (by volume) was calculated for the Neutron Probe (Appendix A) for the peats of Inmoor over the period of study.

2.4.4. FURTHER WORK ON DITCHES.

MEASUREMENT OF THE VARIATION OF COLOUR BETWEEN DITCHES.

Two main ditch sets were sampled, those at Howstean 14 (stream 13), and those on the South East side of the main Howstean Beck (land owned by the Nickerson Group), drainage having occurred in 1984. The Howstean 14 catchment having deposits of Winter Hill peat, whilst the South East side of the beck is largely Wilcocks Series, (this site is referred to as NG). Fig. 2.2 indicates the locations of these sites.

MEASUREMENT OF FLUCTUATING WATER TABLES BY TUBE WELLS.

Three tube well transects were monitored, two at Howstean 14 (Stream 13) and one at Gunnerside Moor, Swaledale. (Samples from Swaledale being provided by F. Booth, North of England Grouse Research Project, The Game Conservancy.)
Fig. 25

Areas of Recent Ditching (1984), Howstea 14 (stream 13) and the SE side of Howstea Beck (NG).
Tube wells were sunk into the peat across transects which dissected two ditches, wells were 50cm deep with holes drilled along their length. Water table measurements were taken from the water surface to the surface of the peat.

2.5 ANALYTICAL TECHNIQUES.

COLOUR

Colour in raw water is in the form of soluble humic and fulvic acids, plus particulate humus and peat materials. Interest here is in the true colour, that is only the soluble proportion of colour and not the additional effect imparted by turbidity (apparent colour).

Turbidity is removed by filtering, under vacuum, through a 0.45 µm milipore filter. Colour is then analyzed by the Spectro-photometric method where water samples are placed in 10mm absorption cells and analyzed for light transmission characteristics compared with distilled water. Analysis takes place across a narrow (10cm or less) spectral band and has an operating range from 400 to 700nm. For this study a standard measurement 400nm was used, multiplied by a factor of 100 to give colour values in Absorption units per metre (Abm⁻¹).

Care must be taken when studying colour records as the method of measuring colour varies from worker to worker and over time. There are three basic ways of measuring
colour, by the Hazen method, by Platinum/Cobalt units, and by the Absorption method.

In the Hazen method, an operator visually compares the water colour with a set of coloured discs which represent the colour of platinum/cobalt solution at different concentrations. The colour of the sample is compared with that of distilled water as viewed through the coloured discs and expressed in Hazen units (H). This method is highly subjective depending as it does on the perception of the operator, McDonald et al., Oct 1987.

The platinum/cobalt unit method again relates the colour of the sample to those of different concentrations of Pt/Co solution, but by much more accurate photospectrometry, against a predetermined scale which is zeroed against a sample of distilled water. Although this method is more objective, the wavelength at which the sample is measured does depend on the wavelength calibration of the Pt/Co scale, which can vary from machine to machine.

Similar problems of 'interpretation' are also encountered when using the absorption method as operators not only use different wavelengths and sizes of cells, but also vary in expressing colour as either 'true' or 'apparent' by this method as well as in the other two methods.
These problems have led to the introduction, by the E.C. of a standard method of colour definition which states that colour should be measured as true colour (having been filtered through 0.45μm filters), by spectrophotometry at a wave length of 400nm expressed in Abm⁻¹; and then converted to Hazen by the conversion factor 1Abm⁻¹ = 15H. The conversion factor derived from a Pt/Co sample of 15 H having been measured by spectrophotometry and found to equal 1 Abm⁻¹.

IRON, ALUMINIUM AND MANGANESE
These were measured by Atomic Absorption Spectroscopy (AAS), iron and manganese were measured using an acetylene flame. For aluminium measurement an acetylene/nitrous oxide flame was used in order to increase the temperature and thus the degree of ionization; potentially obtaining a more accurate result owing to the removal of bands close to the analysis line which may not otherwise have been resolved, the higher temperatures ensuring more complete ionization of aluminium.

Owing to problems with the AAS, later in the research, the method of aluminium measurement changed to that of the Inductively Coupled Plasma Atomic Emission Spectrometer (ICP-AES) system, a system much more accurate than that of AAS.
SOIL AND SAMPLE pH.
Sample pH was measured using a low conductivity pH probe. Soil pH was measured using a solution of 0.01M CaCl₂ and a low conductivity pH probe.

ORGANIC MATTER.
Organic matter was measured by ignition at 425°C for 12 hours or until a constant weight was achieved.

SOIL MOISTURE.
Soil moisture was measured by oven drying at 105°C until a constant weight was achieved.

ANIONS: NITRATE, PHOSPHATE AND SULPHATE
These three anions were measured in an attempt to indicate the potential differences in microbial activity between burnt and non-burnt cores in response to the work of Maltby (1980) and Birch (1958), discussed in Section 1.1.3. Organic acids (colour), NO₃, PO₄ and SO₄ being the primary products of decomposition. As peat contains very low amounts of inorganic matter and therefore few exchange sites, it was postulated that the increased amounts of the three anions in response to increased decomposition in the form of FA and HA (colour), would be apparent in the leachate from water samples.

These were measured using liquid chromatography on the Dionex 4000i. The anion separation column used was an AS4A
and the guard column AG1, the eluent carbonate bicarbonate.

CONDUCTIVITY.
This was measured using a conductivity bridge.

MICROCLIMATE. (WS, A. RAD, T.)
Wind speed was measured using an anemometer, albedo using an albedo meter, radiation by a radiometer and temperature using a thermocouple thermometer.

2.6. STATISTICAL METHODS.
Statistical analysis was carried out using the Statistical Package for Social Science (SPSS). Sample distributions were plotted using histograms and normal curves fitted as a means of checking for normal distribution. For large scale catchment studies the differences between subcatchments were assessed by oneway analysis of variance as data was interval in nature and represented more than 2 independent samples. In addition use was made of the Scheffe multiple comparison test which, although conservative for pairwise comparisons of means, provides information as to which sample populations are significantly different from other sample populations. This enables statements to be made about particular subcatchments for example subcatchment 1 differs significantly from subcatchments 2, 4, 5 etc.
T-tests were used for the following comparisons: burned and non-burned cores both laboratory and naturally burned; block experiments; limed and unlimed cores; for the variables measured - anions, metals, organic matter, pH, colour and soil moisture; burned and non-burned soil temperatures. This allowed the comparison of two independent samples of interval data. Sample populations being different, for example one was burned and the other non-burned.

Relationships between variables, for example colour and iron, were assessed by the use of regression and correlation. Some relationships were found to be strongly correlated, for example iron and colour, where as others were more tenuous indicated by lower levels of correlation, for example Al and colour. Using a scatterplot, standardized predicted values and standardized residuals were plotted enabling residuals which showed large deviations from the regression line to be identified and investigated. Those representing analytical anomalies or those falling outside the general sample population were removed where justified, leading to the improvement of regression relationships. For example iron levels in the base of some cores were high whereas colour levels were low, a factor related to the inorganic matter content of the core rather than as a result of colour levels. Scatterplots also indicate whether any pattern exists between residuals, patterns suggesting that relationships
are not linear in nature. Autocorrelation was tested for using the Durbin-Watson Statistic to test for patterns in residuals, thereby assessing whether the residuals were independent (independent residuals displaying a Durbin-Watson value close to 2). Low values of the Durbin-Watson Statistic indicating positive autocorrelation, that is the relationships are represented by a curve rather than a linear equation. Where Durbin-Watson values were low log transformations were performed on the data to assess whether the relationship would be improved.
CHAPTER THREE

EXPERIMENTAL DATA AND RESULTS

3.0 LARGE SCALE CATCHMENT STUDIES

3.0.0 CATCHMENT CHARACTERISTICS, RESULTS.

Results are given in table 3.0 for Howstean and Inmoor catchment characteristics. Relative size, location and pedological characteristics, are shown Fig. 2.2 for Howstean and Fig. 2.3 for Inmoor.

For the Washburn, catchment characteristics were not measured as there is not a large scale published soil map. However, subjective comparisons have been made with Howstean and Inmoor on the basis of pedological data from the S.S.E.W. 1:250 000 map of Northern England. A rough guide to the pedology of the Washburn is given in map form in Appendix A. The Washburn study concentrates on spatial colour and metal ion variations, rather than catchment characteristics.
## Table 3.0

**Catchment Characteristics, Howsteane and Inmoor.**

<table>
<thead>
<tr>
<th>STREAM ORIGINAL No.</th>
<th>STREAM No.</th>
<th>COLOUR</th>
<th>CATCHMENT MEAN AREA km²</th>
<th>CATCHMENT AREA km²</th>
<th>PEAT %</th>
<th>DITCH LENGTH km</th>
<th>DITCH/CATC- HMENT AREA km²/km²</th>
<th>COMMENTS</th>
</tr>
</thead>
<tbody>
<tr>
<td>H/S 2</td>
<td>1</td>
<td>10.53</td>
<td>1.9400</td>
<td>1.544</td>
<td>79.6</td>
<td>0.0000</td>
<td>0.0000</td>
<td>MLB</td>
</tr>
<tr>
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<td>2.87</td>
<td>0.0518</td>
<td>0.000</td>
<td>0.0</td>
<td>0.0000</td>
<td>0.0000</td>
<td>MLB(s)</td>
</tr>
<tr>
<td>H/S 4</td>
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<td>0.2410</td>
<td>0.003</td>
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<td>1.6200</td>
<td>6.7220</td>
<td>MLB(s)Ditch74</td>
</tr>
<tr>
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<td>4</td>
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<td>0.170</td>
<td>42.3</td>
<td>0.0000</td>
<td>0.0000</td>
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<td>0.0480</td>
<td>0.000</td>
<td>0.0</td>
<td>0.0000</td>
<td>0.0000</td>
<td>MLB(s)</td>
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<tr>
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<td>0.1800</td>
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<tr>
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<td>0.0540</td>
<td>0.008</td>
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<td>1.2150</td>
<td>22.5000</td>
<td>MLDitch 1974</td>
</tr>
<tr>
<td>H/S 10</td>
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<td>0.3710</td>
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</tr>
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<td>1.5455</td>
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<tr>
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<td>0.1730</td>
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<td>55.0</td>
<td>0.0000</td>
<td>0.0000</td>
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<td>0.3500</td>
<td>0.7142</td>
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<td>0.0000</td>
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<td>0.0000</td>
<td>MLB</td>
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<tr>
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<td>0.0660</td>
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<td>0.0000</td>
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<td>0.0352</td>
<td>0.000</td>
<td>0.0</td>
<td>0.0000</td>
<td>0.0000</td>
<td>PP</td>
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<td>0.0432</td>
<td>0.000</td>
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<td>PP</td>
</tr>
<tr>
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<td>0.0864</td>
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</table>

**KEY:**
- H/S = HOWSTEAN
- I/M = INMOOR
- PP = PERMANENT PASTURE
- ML = MOORLAND
- B = BURNED
- B(s) = SLIGHTLY BURNED
- Drained = DRAINED
- Ditch = DITCH & YEAR
3.0.1. ANALYSIS OF DATA AND STATISTICAL RESULTS.

HYPOTHESES CONSIDERED

i) Does colour vary between subcatchments?

ii) Is there a relationship between colour and the area of deep peat per subcatchment?

iii) Is there a relationship between colour and length/unit area of ditch per subcatchment?

iv) Is there a relationship between colour and burning?

v) Does Fe, Al and Mn vary between catchments?

vi) Is there a relationship between Colour and Fe, Al and Mn?

COLOUR VARIANCE BETWEEN SUBCATCHMENTS

It is clear from simple calculations of the means and standard deviations for each subcatchment that colour varies spatially throughout catchments. Results for Howstean (H/S) and Inmoor (I/M) are given in Table 3.1. and for the Washburn (W/B) Table 3.2.

The results are also clearly indicated in plots of mean colour +/- one standard deviation for each catchment; Howstean Fig. 3.0, Inmoor Fig. 3.1, and the Washburn Fig. 3.2.
Table 3.1

HOWSTEAN (H/S) & INMOOR (I/M) SUBCATCHMENTS - TABLE OF MEANS AND
STANDARD DEVIATIONS (std) FOR COLOUR LEVELS WITH REGARD TO SUB-
CATCHMENT (Stream) NUMBER

<table>
<thead>
<tr>
<th>STREAM</th>
<th>COLOUR</th>
<th>COLOUR</th>
<th>No.</th>
<th>ORIGINAL</th>
<th>MEAN</th>
<th>STD</th>
<th>CASES</th>
</tr>
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<tbody>
<tr>
<td>Scarhouse</td>
<td>4.844</td>
<td>1.699</td>
<td>16</td>
<td>I/M 1</td>
<td>16.5159</td>
<td>2.6041</td>
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<td>4.528</td>
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<td>I/M 2</td>
<td>7.8308</td>
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</tr>
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<td>2.871</td>
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<td>I/M 3</td>
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<td>14</td>
</tr>
<tr>
<td>H/S 4</td>
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<td>2.010</td>
<td>19</td>
<td>I/M 4</td>
<td>2.445</td>
<td>3.8144</td>
<td>14</td>
</tr>
<tr>
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<td>6.054</td>
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<td>H/S 6</td>
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<td>3.359</td>
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<td>I/M 6</td>
<td>2.6146</td>
<td>1.8755</td>
<td>13</td>
</tr>
<tr>
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<td>I/M 7</td>
<td>1.5543</td>
<td>0.7115</td>
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</tr>
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<td>H/S 8</td>
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<td>7.656</td>
<td>17</td>
<td>I/M 8</td>
<td>1.5543</td>
<td>0.9493</td>
<td>14</td>
</tr>
<tr>
<td>H/S 9</td>
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<td>6.812</td>
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<tr>
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</table>

**AVE 1-15** 6.484 4.122 250

**AVE16-28** 5.5803 5.3763
Table 3.2

WASHBURN SUBCATCHMENTS - TABLE OF MEANS AND STANDARD DEVIATIONS (Std) FOR COLOUR, ALUMINIUM, IRON AND MANGANESE LEVELS WITH REGARD TO SUBCATCHMENT (STREAM) NUMBER.

<table>
<thead>
<tr>
<th>STREAM No.</th>
<th>MEAN</th>
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<th>CASES</th>
</tr>
</thead>
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<tr>
<td>3</td>
<td>6.1536</td>
<td>3.3355</td>
<td>28</td>
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AVERAGE 1-11: 4.6692 2.8509 224

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AVERAGE 1-11: 0.8784 0.6334 150

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AVERAGE 1-11: 0.2527 0.197 149

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AVERAGE 1-11: 0.09047 0.05595 150
Fig. 3.1 INMOOR SUBCATCHMENTS - MEAN STREAM COLOUR +/- ONE STANDARD DEVIATION (Std).
Fig. 3.2  WASHBURN SUBCATCHMENTS - MEAN STREAM COLOUR +/- ONE STANDARD DEVIATION (Std).

STREAM NUMBER.

--- + 1 Std  ◆ MEAN  --- + 1 Std
Howstean has two noticeably different subcatchments numbers 1 and 13 (HS2 and HS14) each generating the highest colours of the catchment. The Scar House value indicates the mean colour flowing into the reservoir from the aqueduct, representing the final colour after waters from all the H/S and I/M catchments have been mixed. As expected, this value is not dissimilar from that of the average of H/S and I/M, because colour mixes on a one to one ratio. Those differences that do occur are accounted for by the differing volumes of flow from subcatchments, due to their differing catchment areas.

Inmoor similarly exhibits subcatchments with noticeably higher colour values, numbers of 16, 18, and 28 (IM 1, 3 and 13). Only the adjusted mean for No. 28 is plotted on Fig. 3.1, but it can be seen from the table that the unadjusted mean is very high, $\bar{x} = 21.84 \text{ Abm}^{-1}$, $\sigma = 26.59 \text{ Abm}^{-1}$, this data results from extremely high values collected in the summer of 1986 when no flow was present in subcatchment 28 and samples were taken from still water remaining in the intake, colour values of which were as high as 33.8 Abm$^{-1}$ and 75.0 Abm$^{-1}$. As such values are unrepresentative they have been removed to create an adjusted mean for the purposes of statistical analysis. Very low values are apparent for subcatchments 22 and 23 (IM 6 and 7).
At the Washburn a similar variation occurs between subcatchments, higher values being observed in Nos. 3, 5, 6, 8, 9 and 11. It is also apparent that the W/B valley generates much less colour than the H/S and I/M valleys, an expected result in the light of known colour values from their respective treatment works.

The significance of the above variations has been tested by using a one-way analysis of variance, the Scheffe multiple comparison test having been included. The Scheffe test is conservative for pairwise comparisons of means, as it requires larger differences between means to achieve significance, than do other methods, thus the means close to those deemed significant may have been significant, if an alternative method had been used.

The results of the analyses of variance are summarised as follows.

Howstean, F ratio equals 9.3043, significant at p<0.001, subcatchment 1 (HS 2) being significantly different from subcatchments 2, 4, 5, 11, 12, 14 and 15. Subcatchment 13 (HS 14) being significantly different from subcatchments 2, 3, 4, 5, 11, 12, 14 and 15.

Inmoor, F ratio equals 12.1170, significant at p<0.001, subcatchment 16 (IM 1) being significantly different from
subcatchments 19, 20, 21, 22, 23, 24 and 26. Subcatchment 18 (IM 3) significantly different from 19, 21, 22 and 23. Subcatchment 28 (IM.13) may be significantly different, but due to the test used and because the data is adjusted this cannot be proved statistically. Unadjusted subcatchment 28 (IM.13) differs from all others except 16, 17, 18 and 25 significantly.

Washburn, F ratio equals, 9.3370 significant at $p<0.001$ subcatchment 3, differing significantly from subcatchment 1 and subcatchment 11 differing significantly from subcatchments 1, 2, 4, 7 and 10.

Thus it can be clearly stated that spatial differences in colour do occur between the subcatchments of a catchment.

RELATIONSHIP BETWEEN COLOUR AND THE PERCENTAGE AREA OF DEEP PEAT PER SUBCATCHMENT

This relationship is significant, $r = 0.547$, $n = 28$, significant at 0.0026 see Fig. 3.3 Thus it can be said that the greatest amounts of colour within the catchment come from those subcatchments which have 'deep' peat. 'Deep' peat being that defined by the S.S.E.W. as organic deposits greater than 40cm, in this case the Winter Hill Association (1011b). Colour is also generated in catchments at H/S and I/M which do not contain 'deep' peat because they consist of soils with peaty surface horizons
Fig. 3.3  % DEEP PEAT PLOTTED AGAINST MEAN COLOUR VALUES FOR HOWSTEAN AND INMOOR SUBCATCHMENTS.

Colour=3.99+(0.047x%Deep Peat)
\( n=28, r=0.547, \text{ sig } 0.0026, \) using adjusted figures for stream 28.
(not classed as peats), but the amount is significantly less than that generated by peat catchments.

This relationship explains most of the significant differences between the subcatchments mentioned in the previous section, those which are significantly different have large areas of peat deposits. However, some of the variances are unexplained, for example, H/S streams 1 and 13 (HS.2 and HS.14) generate much more colour than streams 8 and 9 (HS.10 and HS 11) but have very similar amounts of peat. It follows therefore that differences must be caused by other factors.

Although no statistical data is available for the Washburn, it is submitted that a similar relationship exists, because streams flowing directly from moorland with deposits of peat are more highly coloured, notably stream 11. Streams 3, 5, 6, 8 and 9 are also high in colour (for the Washburn) as these sampling points lie on the R. Washburn between Thruscross and Fewston reservoirs; the coloured water coming from Thruscross in the form of compensation flow. Thruscross is mainly fed by stream 11, which flows from an area of deep peat, hence the colour.

**RELATIONSHIP BETWEEN COLOUR AND DITCH LENGTH/UNIT AREA**

This relationship is found to be significant, \( r = 0.574, n = 9 \), significant at 0.15, see Fig. 3.4. The relationship would improve if H/S stream 13 (HS.14) could be included in
FIG. 3.4
RELATIONSHIP BETWEEN COLOUR AND LENGTH OF DRAINAGE DITCH PER UNIT AREA OF SUBCATCHMENT.

Colour = 5.00 + (0.164 x ditch)
n = 9, r = 0.574, sig. 0.15
(Catchment 13 omitted due to unmeasured 1984 ditching)

LENGTH OF DRAINAGE DITCH PER UNIT AREA (km/km²)

Catchment No.

1 2 3 4 5 6 7 8 9 10 11 12 13

Colour

0 2 4 6 8 10 12 14
the regression equation as this stream produces high colour and has a high density of ditches. However, it is excluded because the 1984 ditches do not appear on the aerial photographs, and therefore the stated ditch length/unit area is misleading.

Drains on I/M are not included as these are only small scale extensions to the current natural drainage network, created by the Water Authority.

It is proposed that the recent, dense ditching of H/S stream 13 (HS.14) is responsible for its high colour generated, as this cannot be explained only by the percentage of deep peat.

Observations in the field also show that the 1974 ditches have become eroded and base filled with peat from the ditch sides, drainage being impeded. Thus water is removed from these catchments less easily than that of HS stream 13 (HS.14) where ditches are 'clean' and drainage is rapid.

RELATIONSHIP BETWEEN COLOUR AND THE PRESENCE OF BURNING
No significant relationship is found, F ratio equals 0.5769, not significant at 0.4544. This is not surprising as the measure of burning is very crude!

It is postulated however, that a relationship does exist, since subcatchments which experience regular burning
generate high amounts of colour compared with non-burnt peat catchments having similar areas of peat. This may explain the variance of streams 1, 16, 18 and possibly 28 (HS 2, IM 1, 3 and 13).

Catchment 11 on the Washburn is also burnt which may increase its colour generating capacity.

SPATIAL VARIATION OF Fe, Al AND Mn BETWEEN SUBCATCHMENTS AND RELATIONSHIP WITH COLOUR.
Results for the means and standard deviations of the above metal ions are given in Table 3.2. Graphs of these values are also given in Fig. 3.5. It is clearly visible that as with colour there is a spatial variation between subcatchments for Fe, Al and Mn.

Iron varies significantly from subcatchment to subcatchment, oneway analysis of variance F ratio = 14.2004 significant at p<0.001. Scheffe revealing that Stream 11 varies significantly from all other streams. A clear indication that Fe levels are related to upland peat catchments and colour. Regression analysis shows that this relationship is significant r = 0.713, N = 147, significantly at p<0.001.

Aluminium levels vary significantly between subcatchments, F ratio = 3.2585, significant at p<0.001. However, regression analysis whilst revealing a significant
Fig. 3.5

WASHBURN SUBCATCHMENTS - MEAN STREAM ALUMINIUM +/- ONE STANDARD DEVIATION (Std).

STREAM NUMBER

WASHBURN SUBCATCHMENTS - MEAN STREAM MANGANESE +/- ONE STANDARD DEVIATION (Std).

STREAM NUMBER

WASHBURN SUBCATCHMENTS - MEAN STREAM IRON +/- ONE STANDARD DEVIATION (Std).

STREAM NUMBER
relationship ($r = 0.317$, $n = 148$, significantly $p<0.001$) indicates that a negative relationship exists between colour and aluminium, for this catchment. This is thought to be because colour values are relatively low in this catchment, and that values from moorland flow are being overshadowed by those of lower forested catchments. Scheffe indicates that stream 7 is significantly different from stream 10.

Manganese levels also differ between subcatchments, $F$ ratio $= 10.6105$, significant at $p<0.001$. Colour is negatively related to Mn, ($r = 0.2779$, $n = 148$ significant at $p<0.001$), again this is thought to be due to the relatively low colour levels generated in the Washburn, and the influence of large values from streams 1 and 2 overshadowing from of 10 and 11. Stream 1 differs significantly from stream 9 and 6, and stream 2 differs from all others (Scheffe), both catchments are forested.

CLEAR FELLING: COMMENTS

It was initially thought that colours, may be high around Redshaw Gill, hence the large number of sampling points. However, the clear felling in this area appears to have had little affect on colour production, streams 4 and 7 producing relatively little colour. This may be because the area of subcatchment concerned has not so far replaced any moisture deficit resulting from afforestation. A more likely explanation however, is that the area concerned is
of the Rivington soil series (541g) which does not contain large deposits of peat.

3.1. THE EFFECT OF MOORLAND BURNING ON COLOUR IN RAW WATER

3.1.0 INITIAL SMALL SCALE LEACHING AND SHAKING EXPERIMENTS.

LEACHED SAMPLES

Results of colour and metal ions by depth are given in Table 3.3.

Colour clearly differs between burnt and non-burnt cores, the mean for burnt cores is 125.69 Abm"1 and for non-burnt cores 41.74 Abm"1, significant at p<0.004 (t-test, one tailed), burnt cores producing greater amounts of colour (signif. at p<0.008, two tailed); maximum recorded colour for burnt cores being 800 Abm"1 and for non-burnt cores 148.5 Abm"1. In both core types the greatest production is in the upper layers of the core.

Metal ion content also differs between burnt and non-burnt cores. For iron, the mean for burn cores equals 6.53ppm. and for non-burnt is 2.48ppm., significant at p<0.012 (t-test), burnt cores producing greater amounts (signif. at p<0.006). Mean content for aluminium equals 8.95ppm. (B) and 5.14ppm. (NB) significant at p<0.007, greater amounts
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<th>IRON</th>
<th>ALUMINIUM</th>
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<td>6.17</td>
<td>0.040</td>
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| NONBURNT CORES | | | | |
| IMNB 5 LITTER | 137.4 | 3.21 | 27.54 | 0.535 |
| IMNB 5 s-LITTER | 34.9 | 2.62 | 4.19 | 0.026 |
| IMNB 5 4-9 | 91.9 | 3.83 | 4.30 | 0.030 |
| IMNB 5 9-14 | 83.9 | 3.40 | 3.70 | 0.500 |
| IMNB 5 >14 | 29.0 | 1.03 | 5.39 | 0.000 |
| IMNB 6 LITTER | 62.1 | 2.91 | 13.12 | 0.013 |
| IMNB 6 s-LITTER | 0.0 | 0.00 | 0.00 | 0.000 |
| IMNB 6 4-9 | 91.8 | 2.79 | 4.88 | 0.020 |
| IMNB 6 9-14 | 68.6 | 1.65 | 0.00 | 0.000 |
| IMNB 6 >14 | 25.6 | 2.15 | 4.21 | 0.010 |
| IMNB 7 LITTER | 38.2 | 2.06 | 1.75 | 0.052 |
| IMNB 7 s-LITTER | 39.7 | 1.87 | 2.99 | 0.034 |
| IMNB 7 4-9 | 84.6 | 3.22 | 3.06 | 0.030 |
| IMNB 7 9-14 | 61.1 | 2.53 | 4.87 | 0.010 |
| IMNB 7 >14 | 10.4 | 1.05 | 3.45 | 0.010 |
| IMNB 8 LITTER | 26.3 | 2.31 | 1.98 | 0.000 |
| IMNB 8 s-LITTER | 51.1 | 2.21 | 5.51 | 0.032 |
| IMNB 8 4-9 | 16.6 | 1.97 | 0.00 | 0.000 |
| IMNB 8 9-14 | 50.2 | 2.35 | 4.86 | 0.020 |
| IMNB 8 >14 | 9.2 | 2.00 | 3.47 | 0.009 |
| HSNB 9 LITTER | 24.2 | 0.00 | 2.94 | 0.000 |
| HSNB 9 1-8 | 7.6 | 2.49 | 2.01 | 0.067 |
| HSNB 9 >8 | 11.5 | 2.73 | 1.90 | 0.010 |
| HSNB 10 LITTER | 64.6 | 0.00 | 8.01 | 0.132 |
| HSNB 10 1-8 | 13.9 | 2.02 | 2.81 | 0.064 |
| HSNB 10 >8 | 13.8 | 1.85 | 8.53 | 0.000 |
| HSNB 11 LITTER | 29.5 | 2.03 | 3.37 | 0.000 |
| HSNB 11 1-8 | 17.9 | 2.57 | 4.71 | 0.032 |
| HSNB 11 >8 | 5.5 | 1.71 | 3.07 | 0.010 |
| HSNB 12 LITTER | 52.7 | 5.25 | 4.46 | 0.050 |
| HSNB 12 1-8 | 31.5 | 4.01 | 7.86 | 0.072 |
| HSNB 12 >8 | 8.7 | 2.22 | 5.30 | 0.010 |
being produced by burnt cores (signif. at p<0.0014). For manganese a similar pattern exists, burnt cores producing more than non-burnt cores, 0.18ppm. (B) and 0.07ppm. (NB), significant at p<0.048 (t-test), burnt cores producing greater amounts (signif. at p<0.0216).

A significant relationship also exists between colour and the levels of Fe, Al, and Mn. Regression equations equalling:

\[ \text{Fe} = 1.20 + (0.04 \times \text{colour}). \] (Signif. at p<0.001).
\[ \text{Al} = 5.69 + (0.02 \times \text{colour}). \] (Signif. at p<0.001).
\[ \text{Mn} = 0.01 + (0.004 \times \text{colour}). \] (Signif. at p<0.0162).

**SHAKEN SAMPLES**

Results are given in Table 3.4.

Again, colour produced clearly differs between burnt (B) and non-burnt (NB) cores, means equalling 41.2 Abm\(^{-1}\) and 20.5 Abm\(^{-1}\) respectively, t-test significant at p<0.027. B cores generating significantly more colour, (signif. at p<0.0135).

For metals, cores produce differing amounts of Fe., means equalling 3.26ppm. (B) and 1.79ppm. (NB), (signif. at p<0.001), burnt cores producing significantly more (signif. at p<0.001). However, differences in values for Al. and Mn. are not significant, Al. means equalling 4.95ppm. (B) and 3.67ppm. (NB) (not signif. at p<0.246), Mn. means
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<th>ALUMINIUM</th>
<th>MANGANESE</th>
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</table>

**NONBURNT CORES**

| INMB 5      | LITTER| 21.9  | 1.23 | 7.34      | 0.098     |
| INMB 5      | s-LITTER| 12.9  | 1.10 | 1.90      | 0.008     |
| INMB 5      | 4-9   | 39.0  | 2.26 | 4.11      | 0.047     |
| INMB 5      | 9-14  | 28.4  | 2.15 | 3.18      | 0.020     |
| INMB 5      | >14   | 17.3  | 2.30 | 2.43      | 0.014     |
| INMB 6      | LITTER| 23.9  | 1.58 | 7.84      | 0.108     |
| INMB 6      | s-LITTER| 17.9  | 1.33 | 3.39      | 0.019     |
| INMB 6      | 4-9   | 36.6  | 1.43 | 3.47      | 0.019     |
| INMB 6      | 9-14  | 27.1  | 1.03 | ---       | ---       |
| INMB 6      | >14   | 14.8  | 1.03 | 2.38      | 0.014     |
| HSNB 9      | LITTER| 15.3  | 2.49 | 3.43      | 0.073     |
| HSNB 9      | 1-8   | 29.5  | ---  | 4.55      | 0.034     |
| HSNB 9      | >8    | 3.2   | 3.31 | 1.70      | 0.005     |
| HSNB10      | LITTER| 14.9  | 1.13 | ---       | 0.027     |
| HSNB10      | 1-8   | 20.3  | 2.37 | 3.48      | 0.028     |
| HSNB10      | >8    | 4.3   | 2.11 | 2.23      | 0.010     |
equalling 0.08ppm. (B) and 0.03ppm. (NB) (not signif. at p<0.291). The relationship between colour and metal ions was not explored for reasons outlined below.

It was also noted that colour values between leached samples and shaken samples were significantly different (for groups including both B and NB cores; leached samples having a mean of 96.1 Abm⁻¹ and shaken 41.2 Abm⁻¹ (signif at p<0.008 (t-test)). The same is probably true of metal ions since there is a significant relationship between colour and metal ions.

CONTINUOUS LEACHING EXPERIMENTS

Results of these are given in Figs. 3.6 - 3.9. It can be clearly seen that the potential for colour and associated metal ion generation is high for even a small peat sample (25g.), in both B and NB cores; indicating that colour production, once started, has a long term potential effect.

3.1.1. LARGE SCALE FIELD CORE EXPERIMENTS

A number of such experiments were conducted, reported individually and discussed collectively, where relevant.

Results discussed in the following sections are given in Table 3.5 - April 1988; Table 3.6 - August 1988, Table 3.7 - January 1989 and Table 3.8 - April 1989.
Fig 3.6 LEACHED CORES, COLOUR VERSUS NUMBER OF DAYS FOR BURNT AND NONBURNT CORES.

Fig 3.7 LEACHED CORES, IRON VERSUS NUMBER OF DAYS FOR BURNT AND NONBURNT CORES.
**Fig 3.8**

LEACHED CORES, ALUMINIUM VERSUS NUMBER OF DAYS FOR BURNT AND NONBURNT CORES.

**Fig 3.9**

LEACHED CORES, MANGANESE VERSUS NUMBER OF DAYS FOR BURNT AND NONBURNT CORES.
### TABLE 3.5

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<th>SO4</th>
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<th>% OM</th>
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<th>% OM</th>
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### TABLE 3.8

#### APRIL 1989

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<th>TYPE</th>
<th>COL</th>
<th>Fe</th>
<th>A1</th>
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<th>Cl</th>
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<th>SO4</th>
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<th>% OM</th>
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### KEY

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<td>IMB</td>
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<td>HSNB</td>
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<td></td>
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<tr>
<td>IMNB</td>
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<th>% SOIL MOISTURE</th>
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<tr>
<td>IMB</td>
<td>182.3</td>
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<tr>
<td>HSNB</td>
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<td>HSNB</td>
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<td>IMNB</td>
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<td>HSNB</td>
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<td>IMB</td>
<td>182.3</td>
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<td>IMNB</td>
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<tr>
<td>IMNB</td>
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</table>
VARIATION IN COLOUR BETWEEN BURNT AND NON-BURNT CORES

April 1988: Results for these cores are given in Figs. 3.8 to 3.11. No statistical variation was found in colour between burnt and non-burnt cores (Table 3.5), by using the students t-test, for the following groups: burnt cores (HS & IM) vs non-burnt cores, BHS vs BIM, NBHS vs NBIM, BHS vs BIM, NBHS vs NBIM, BHS vs NBHS and BIM vs NBIM. Such groups being used for all variables discussed, significance level 90%/0.10.

August 1988: Results given in Figs. 3.12 - 3.15. From Table 3.6 it is clear that cores from BHS produce a mean colour value greater than those from NBHS, BIM and NBIM. This is supported by statistical results, using students t-test, the following tests being significant.

Significance (two tailed)

<table>
<thead>
<tr>
<th>Test</th>
<th>Significance</th>
</tr>
</thead>
<tbody>
<tr>
<td>BHS vs BIM, NBHS, NBIM</td>
<td>0.003</td>
</tr>
<tr>
<td>BHS vs BIM</td>
<td>0.003</td>
</tr>
<tr>
<td>BHS vs NBHS</td>
<td>0.002</td>
</tr>
<tr>
<td>(B(HS + IM) vs NB(HS + IM)</td>
<td>0.005</td>
</tr>
</tbody>
</table>

Statistical analysis suggests that burnt cores from HS + IM are significantly different from non-burnt cores, closer examination of the data indicates that this is not the case however, as large values for BHS distort the mean for the burnt group, this is illustrated by the test BHS vs BIM, where colour values are shown to be significantly different.
Fig. 3.8(c)

COLOUR VARIATION WITH DEPTH FOR BURNT CORES,
HOWSTEAN, APRIL 1988.

Fig. 3.9(a)

COLOUR VARIATION WITH DEPTH FOR NONBURNT CORES,
HOWSTEAN, APRIL 1988.
Fig. 3.10

COLOUR VARIATION WITH DEPTH FOR BURNT CORES.

Fig. 3.11

COLOUR VARIATION WITH DEPTH FOR NONBURNT CORES.
Fig. 3.12

**COLOUR VARIATION WITH DEPTH FOR BURNT CORES, HOWSTEAN, AUGUST 1988.**

![Graph showing colour variation with depth for burnt cores.](image)

Fig. 3.13

**COLOUR VARIATION WITH DEPTH FOR NONBURNED CORES, HOWSTEAN, AUGUST 1988.**

![Graph showing colour variation with depth for nonburnt cores.](image)
Fig. 3.14

COLOUR VARIATION WITH DEPTH FOR BURNT CORES,

Fig. 3.15

COLOUR VARIATION WITH DEPTH FOR NONBURNT CORES,
January 1989: Results given in Figs. 3.16 - 3.19. Table 3.7 indicates that there is a wide range of mean colour values between the core groups concerned, statistical results showing several significant variations.

Significance (two tailed)

B (HS + IM) vs NB (HS + IM) 0.001
BHS vs BIM, NBIM, NBHS 0.012
BHS vs BIM 0.073
BHS vs NBHS 0.004
BIM vs NBIM 0.082

Burnt cores produce greater amounts of colour than non-burnt cores and in turn BHS produces more colour than BIM, there being no significant difference between colour generated by NBHS and NBIM.

April 1989: Results given in Figs. 3.20 - 3.30. Table 3.8 indicates that cores from BHS produce a greater mean colour value than those from NBHS, BIM and NBIM. Statistical tests show this to be the case.

Significance (two tailed)

BHS vs BIM, NBHS, NBIM 0.002
BHS vs BIM 0.002
BHS vs NBHS 0.004
(B(HS + IM) vs NB(HS + IM) 0.005)

As in the April 1988 cores, there appears to be a significant difference between B(HS + IM) vs NB(HS + IM) however, this is not so, as large values from BHS distort
Fig. 3.16

COLOUR VARIATION WITH DEPTH FOR BURNT CORES,
HOWSTEAN, JANUARY 1989.

Fig. 3.17

COLOUR VARIATION WITH DEPTH FOR NONBURNT CORES,
HOWSTEAN, JANUARY 1989.
Fig. 3.18

COLOUR VARIATION WITH DEPTH FOR BURNT CORES.
INMOOR, JANUARY 1989.

Fig. 3.19

COLOUR VARIATION WITH DEPTH FOR NONBURNT CORES.
INMOOR, JANUARY 1989.
Fig. 3.20

COLOUR VARIATION WITH DEPTH FOR BURNT CORES,
HOWSTEAN, APRIL 1989.

Fig. 3.21

COLOUR VARIATION WITH DEPTH FOR NONBURNT CORES,
HOWSTEAN, APRIL 1989.
Fig. 3.22

COLOUR VARIATION WITH DEPTH FOR BURNT CORES,
INMOOR, APRIL 1989.

![Graph showing colour variation with depth for burnt cores.]

Fig. 3.23

COLOUR VARIATION WITH DEPTH FOR NONBURNT CORES,
INMOOR, APRIL 1989.

![Graph showing colour variation with depth for nonburnt cores.]

_COLOR VALUE_ 0 is missing value.
the group, there being no significant difference between BIM and NBHS and NBIM.

RELATIONSHIP BETWEEN IRON AND COLOUR

The relationship between iron and colour was measured for two core sets, August 1988 and April 1989. In both cases iron was found to be significantly related to colour. Relationships are shown Figs. 3.24 and 3.25.

Significance (two tailed)

<table>
<thead>
<tr>
<th></th>
<th>August 1988</th>
<th>April 1989</th>
</tr>
</thead>
<tbody>
<tr>
<td>Students t-test</td>
<td></td>
<td></td>
</tr>
<tr>
<td>B(HS + IM) vs NB(HS + IM)</td>
<td>(0.126)</td>
<td>(0.126)</td>
</tr>
<tr>
<td>BHS vs BIM, NBIM, NBHS</td>
<td>0.010</td>
<td>0.019</td>
</tr>
<tr>
<td>BHS vs BIM</td>
<td>0.004</td>
<td>0.013</td>
</tr>
<tr>
<td>BHS vs NBHS</td>
<td>0.068</td>
<td>(0.217)</td>
</tr>
</tbody>
</table>

(         ) not significant.

Tests between B(HS + IM) vs NB(HS + IM) are not significant as in these sets of cores, BIM produces similar amounts of iron to non-burnt cores. The mean for the burnt group is thus lowered so that it is not significantly different from non-burnt cores, this is also the case with colour comparison, in these sets of cores.

For April 1989, BHS vs NBHS does indicate a difference but it is not significant see Table 3.8. All other statistical tests proved to be not significant, there being no difference between BIM, NBIM and NBHS.
FIG. 3.24


Regression line for Nonburnt (NB) cores
\[ \text{Fe} = -0.0214 + (0.0490 \times \text{Colour}) \]
\( n = 25, r = 0.708, p < 0.001, DW = 1.64 \)

Regression line for Burnt (B) cores
\[ \text{Fe} = 0.179 + (0.00144 \times \text{Colour}) \]
\( n = 23, r = 0.807, p < 0.001, DW = 1.74 \)
FIG. 3.25

RELATIONSHIP BETWEEN IRON AND COLOUR FOR CORES TAKEN DURING APRIL 1989.

Regression line for Nonburnt (NB) cores
\[ \text{Fe} = -0.211 + (0.0489 \times \text{Colour}) \]
\( n = 23, r = 0.958, p < 0.001, DW = 1.42 \)

Regression line for Burnt (B) cores
\[ \text{Fe} = 0.0470 + (0.0178 \times \text{Colour}) \]
\( n = 22, r = 0.920, p < 0.001, DW = 2.19 \)
Iron is plotted against depth in Figs. 4.6, comparison with Fig. 4.5 indicates, with only a few exceptions, the similarity between the pattern of iron and colour with depth.

**RELATIONSHIP BETWEEN COLOUR AND ALUMINIUM**

The relationship for aluminium was considered using results from August 1988 and April 1989 cores. The relationship for August 1988 B + NB cores and April 1989 NB was found not to be significant, whilst the relationship for April 1989 B was significant, Fig. 3.26.

Few significant differences were noted between BHS, BIM, NBIM and NBHS for Al indicated in Fig. 3.27, exceptions being:

<table>
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<tr>
<th>Comparison</th>
<th>Significance</th>
<th>Date</th>
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</thead>
<tbody>
<tr>
<td>BHS vs BIM</td>
<td>Signif 0.082</td>
<td>August 1988</td>
</tr>
<tr>
<td>BHS vs NBHS</td>
<td>Signif 0.102</td>
<td>April 1989</td>
</tr>
<tr>
<td>BIM vs NBIM</td>
<td>Signif 0.084</td>
<td>August 1988</td>
</tr>
<tr>
<td>NBHS vs NBIM</td>
<td>Signif 0.083</td>
<td>April 1989</td>
</tr>
</tbody>
</table>

All other groups tested indicate no significant difference. Of the above groups, only the first two follow the same pattern as that for colour.
RELATIONSHIP BETWEEN ALUMINIUM AND COLOUR FOR CORES TAKEN DURING APRIL 1989.

Regression line for Burnt (B) cores
\[ Al = 0.140 + (0.00373 \times \text{Colour}) \]
\[ n = 24, r = 0.784, p < 0.001, DW = 1.95 \]

ALUMINIUM VARIATION WITH DEPTH FOR CORES TAKEN IN AUGUST 1988. (Average of three cores per line.)
RELATIONSHIP BETWEEN COLOUR AND MANGANESE

Results show that manganese is negatively correlated with colour. August 1988 results are given Fig. 3.28 for B cores, $Mn = 0.130 - (0.00153 \times \text{colour}) \ p<0.03$, for NB no significant relationship was found. A similar pattern of results were obtained from April 1989 cores, although they were not significant.

Mean differences in manganese, between cores, are shown in Tables 3.6 and 3.8 and follow broadly the same relationship as above, but only two statistical tests bear this out.

B(HS + IM) vs NB(HS + IM) Signif 0.087 August 1988
NBHS vs NBIM Signif 0.004 April 1989

In both cases low colours produce high manganese values. Only one exception to this arises, (BHS vs NBHS signif 0.077, August 1988) but in the light of the above correlation this is unlikely to be due to colour. All other tests show no significant variation.

RELATIONSHIP BETWEEN COLOUR AND NITRATE, PHOSPHATE AND SULPHATE.

Work on the relationships between colour and NO$_3$ and SO$_4$ (August 1988, April 1989) proved to be largely unsuccessful. Regression equations for both NO$_3$ and SO$_4$ were found to be not significant and t-tests between groups of cores did not reveal higher significant values for burnt cores, exceptions being BHS vs NBHS for SO$_4$ P<0.02, (April

Regression line for Burnt (B) cores
Mn = 0.130 - (0.00153 x Colour)
n = 27, r = 0.421, p < 0.029, DW = 1.57

Δ NB
△ B
1989 cores) and BHS vs BIM, BHS vs NBIM, NBHS, and BIM P<0.09, (April 1989 cores), changing nitrate levels mirroring the increase in colour levels.

Efforts to establish relationships between PO₄ and colour proved to be more successful, results from April 1989 cores demonstrating a positive correlation between PO₄ and colour for burned cores, PO₄ = 0.525 + (0.00663 x colour), P<0.017, DW =1.89, r=0.46. However, results from August 1988 cores did not confirm this relationship. T-tests revealed several significant differences between PO₄ levels between burnt and non-burnt cores, burnt cores showing higher levels.

<table>
<thead>
<tr>
<th>Test</th>
<th>August 1988</th>
<th>April 1989</th>
</tr>
</thead>
<tbody>
<tr>
<td>B(HS + IM) vs NB(HS + IM)</td>
<td>0.027</td>
<td>0.043</td>
</tr>
<tr>
<td>BIM vs BIM, NBIM, NBHS</td>
<td>(0.861)</td>
<td>0.004</td>
</tr>
<tr>
<td>BIM vs BHS</td>
<td>(0.435)</td>
<td>0.046</td>
</tr>
<tr>
<td>BHS vs NBHS</td>
<td>cannot calc</td>
<td>(0.197)</td>
</tr>
<tr>
<td>BIM vs NBIM</td>
<td>(0.102)</td>
<td>(0.101)</td>
</tr>
<tr>
<td>NBHS vs NBIM</td>
<td>cannot calc</td>
<td>0.039</td>
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**RELATIONSHIP BETWEEN WATER SAMPLE PH AND COLOUR**

Measurements used were from January 1989 and April 1989 cores. Regression analysis for both sets of cores showed no significant relationship between colour and pH.
Statistical t-tests between groups of cores revealed no evidence of increased pH in burnt cores, apart from 3 exceptions.

**Significance (two tailed)**

<table>
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<tr>
<th></th>
<th>Jan 1989</th>
<th>April 1989</th>
</tr>
</thead>
<tbody>
<tr>
<td>B(HS + IM) vs NB(HS + IM)</td>
<td>0.049</td>
<td>(0.907)</td>
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<tr>
<td>BHS vs BIM, NBIM, NBHS</td>
<td>(0.809)</td>
<td>(0.999)</td>
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<tr>
<td>BIM vs BHS</td>
<td>(0.195)</td>
<td>(0.935)</td>
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<tr>
<td>BHS vs NBHS</td>
<td>(0.998)</td>
<td>(0.845)</td>
</tr>
<tr>
<td>BIM vs NBIM</td>
<td>0.030</td>
<td>(0.972)</td>
</tr>
<tr>
<td>NBHS vs NBIM</td>
<td>0.051</td>
<td>(0.763)</td>
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</tbody>
</table>

( ) not significant.

**RELATIONSHIP BETWEEN CONDUCTIVITY AND COLOUR**

Water sample conductivity was measured for January 1989, and April 1989 cores. Regression equations revealed no significant correlation between colour and conductivity. T-tests between groups of cores also showed no significant differences relating to increases in colour.

**RELATIONSHIP BETWEEN COLOUR AND SOIL MOISTURE**

This relationship was tested using data from April 1988, January 1989 and April 1989 cores. Regression analysis revealed no significant relationship between soil moisture and colour, the range of soil moistures for all core groups being very narrow, between 70 and 90%. T-tests between groups of cores revealed significant variations, the reasons for which can be clearly seen in Fig. 3.29 for April 1988, other cores sets display similar patterns. T-test results are listed over leaf:-
Fig. 3.29

% BOIL MOISTURE VARIATION WITH DEPTH FOR CORES
TAKEN IN APRIL 1989. (AVERAGE OF THREE CORES PER LINE.)

DEPTH (cm)

SOIL MOISTURE

LITTER  5-10  11-15  16-20  20-25
Significance (two tailed)

<table>
<thead>
<tr>
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<th>January 1989</th>
<th>April 1989</th>
</tr>
</thead>
<tbody>
<tr>
<td>B(HS + IM) vs NB(HS + IM)</td>
<td>(0.795)</td>
<td>(0.515)</td>
<td>0.002</td>
</tr>
<tr>
<td>BHS vs BIM, NBHS, NBIM</td>
<td>(0.068)</td>
<td>0.070</td>
<td>0.029</td>
</tr>
<tr>
<td>BHS vs BIM</td>
<td>0.002</td>
<td>0.062</td>
<td>(0.606)</td>
</tr>
<tr>
<td>BHS vs NBHS</td>
<td>0.008</td>
<td>(0.498)</td>
<td>(0.103)</td>
</tr>
<tr>
<td>BIM vs NBIM</td>
<td>(0.137)</td>
<td>(0.879)</td>
<td>0.009</td>
</tr>
<tr>
<td>NBHS vs NBIM</td>
<td>(0.214)</td>
<td>0.033</td>
<td>0.030</td>
</tr>
</tbody>
</table>

( ) not significant.

**RELATIONSHIP BETWEEN COLOUR AND ORGANIC MATTER**

The relationship between April 1988, 1989 and January 1989 burned and non-burned cores was tested and all regression analyses indicated no significant relationship between colour and organic matter. Data for April 1988 burned cores produced the relationship:

\[ \text{Colour} = -1.91 + (0.883 \times \text{OM}) \quad r=0.36, \quad Dw=2.17, \quad p<0.055 \]

but this falls outside the acceptance level of 95% significance, see Fig. 3.30. Performing log transformations on the data did not improve the level of significance.

T-tests revealed some degree of variance between certain core sets, mostly explained by increased amounts of inorganic matter at the base of some cores, which affected their mean organic matter values. Values of organic matter with depth are shown in Figs. 4.9 and 4.10. T-test results are given following the figure.
FIG. 3.30

COLOUR VERSUS % ORGANIC MATTER FOR CORES TAKEN DURING APRIL 1988.
Significance (two tailed)
April 1988 January 1989 April 1989

B(HS + IM) vs NB(HS + IM) (0.483) (0.698) 0.048
BHS vs BIM, NBIM, NBIM (0.902) (0.120) 0.001
BHS vs BIM (0.473) (0.149) 0.032
BHS vs NBHS 0.094 (0.329) 0.001
BIM vs NBIM 0.058 (0.805) (0.245)
NBHS vs NBIM 0.011 (0.574) 0.042

( ) not significant.

3.1.2 LABORATORY EXPERIMENTS OF BURNING CORES AT DIFFERENT TEMPERATURES

Mean results for variables measured are shown in Table 3.9.

VARIATION IN COLOUR BETWEEN NON-BURNT AND CORES BURNT AT 300, 600 AND 800°C

T-test for the following groups of cores were carried out, the same groups were used for all variables measured in this experiment, significance level being set at 90%, p<0.10.

Significance level (two tailed)

<table>
<thead>
<tr>
<th></th>
<th>Leached Colour</th>
<th>Shaken Colour</th>
</tr>
</thead>
<tbody>
<tr>
<td>B(300,600,800) vs NB</td>
<td>(0.928)</td>
<td>(0.135)</td>
</tr>
<tr>
<td>B300 vs NB</td>
<td>(0.377)</td>
<td>(0.120)</td>
</tr>
<tr>
<td>B600 vs NB</td>
<td>(0.666)</td>
<td>(0.311)</td>
</tr>
<tr>
<td>B800 vs NB</td>
<td>(0.492)</td>
<td>(0.455)</td>
</tr>
<tr>
<td>B300 vs B600</td>
<td>(0.223)</td>
<td>(0.613)</td>
</tr>
<tr>
<td>B300 vs B800</td>
<td>(0.159)</td>
<td>(0.476)</td>
</tr>
<tr>
<td>B600 vs B800</td>
<td>(0.798)</td>
<td>(0.827)</td>
</tr>
</tbody>
</table>

( ) not significant,
### TABLE 3.9

**TABLE OF MEAN RESULTS FOR LABORATORY BURNT CORES.**

<table>
<thead>
<tr>
<th>LEACHED SAMPLES</th>
<th>%SM af</th>
<th>%OM</th>
<th>pH soil</th>
<th>%SM ar</th>
<th>pH smpl</th>
<th>COND</th>
<th>COL</th>
<th>Fe</th>
<th>Al</th>
<th>Mn</th>
<th>Cl</th>
<th>NO3</th>
<th>SO4</th>
<th>PO4</th>
</tr>
</thead>
<tbody>
<tr>
<td>NB</td>
<td>83.42</td>
<td>89.26</td>
<td>2.36</td>
<td>50.27</td>
<td>2.96</td>
<td>273.00</td>
<td>11.13</td>
<td>0.3115</td>
<td>0.2957</td>
<td>0.1215</td>
<td>15.82</td>
<td>9.30</td>
<td>95.85</td>
<td>0.45</td>
</tr>
<tr>
<td>300</td>
<td>66.57</td>
<td>86.28</td>
<td>2.36</td>
<td>78.44</td>
<td>3.34</td>
<td>274.58</td>
<td>13.84</td>
<td>0.2417</td>
<td>0.2560</td>
<td>0.0708</td>
<td>14.55</td>
<td>7.98</td>
<td>54.97</td>
<td>1.15</td>
</tr>
<tr>
<td>600</td>
<td>74.20</td>
<td>88.52</td>
<td>2.28</td>
<td>84.63</td>
<td>2.95</td>
<td>209.25</td>
<td>10.19</td>
<td>0.2152</td>
<td>0.2413</td>
<td>0.0719</td>
<td>13.98</td>
<td>11.01</td>
<td>58.04</td>
<td>0.71</td>
</tr>
<tr>
<td>800</td>
<td>70.29</td>
<td>89.89</td>
<td>2.33</td>
<td>84.90</td>
<td>2.58</td>
<td>216.11</td>
<td>9.68</td>
<td>0.2488</td>
<td>0.2219</td>
<td>0.1136</td>
<td>15.44</td>
<td>3.31</td>
<td>69.04</td>
<td>0.70</td>
</tr>
<tr>
<td>BURNT, all</td>
<td>70.35</td>
<td>88.29</td>
<td>2.35</td>
<td>82.66</td>
<td>2.92</td>
<td>234.88</td>
<td>11.31</td>
<td>0.2360</td>
<td>0.2413</td>
<td>0.8540</td>
<td>14.61</td>
<td>7.67</td>
<td>59.99</td>
<td>0.87</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>SHAKEN SAMPLES</th>
<th>%SM af</th>
<th>%OM</th>
<th>pH soil</th>
<th>%SM ar</th>
<th>pH smpl</th>
<th>COND</th>
<th>COL</th>
<th>Fe</th>
<th>Al</th>
<th>Mn</th>
<th>Cl</th>
<th>NO3</th>
<th>SO4</th>
<th>PO4</th>
</tr>
</thead>
<tbody>
<tr>
<td>NB</td>
<td>83.42</td>
<td>89.26</td>
<td>2.36</td>
<td>50.27</td>
<td>2.96</td>
<td>14.76</td>
<td>0.3033</td>
<td>0.0801</td>
<td>0.0223</td>
<td>15.65</td>
<td>5.48</td>
<td>17.17</td>
<td>1.43</td>
<td></td>
</tr>
<tr>
<td>300</td>
<td>66.57</td>
<td>86.28</td>
<td>2.36</td>
<td>78.44</td>
<td>3.34</td>
<td>19.43</td>
<td>0.3655</td>
<td>0.1484</td>
<td>0.0304</td>
<td>17.11</td>
<td>7.24</td>
<td>18.48</td>
<td>0.90</td>
<td></td>
</tr>
<tr>
<td>600</td>
<td>74.20</td>
<td>88.52</td>
<td>2.28</td>
<td>84.63</td>
<td>2.95</td>
<td>17.73</td>
<td>0.4496</td>
<td>0.1263</td>
<td>0.0317</td>
<td>15.61</td>
<td>6.09</td>
<td>16.97</td>
<td>0.90</td>
<td></td>
</tr>
<tr>
<td>800</td>
<td>70.29</td>
<td>89.89</td>
<td>2.33</td>
<td>84.90</td>
<td>2.58</td>
<td>16.99</td>
<td>0.3027</td>
<td>0.0775</td>
<td>0.0227</td>
<td>16.14</td>
<td>4.87</td>
<td>17.20</td>
<td>0.89</td>
<td></td>
</tr>
<tr>
<td>BURNT, all</td>
<td>70.35</td>
<td>88.29</td>
<td>2.35</td>
<td>82.66</td>
<td>2.92</td>
<td>18.05</td>
<td>0.3747</td>
<td>0.1161</td>
<td>0.0285</td>
<td>16.35</td>
<td>6.12</td>
<td>17.61</td>
<td>0.90</td>
<td></td>
</tr>
</tbody>
</table>

**KEY**

- **NB**
  - NONBURNT
- **300**
  - BURNT AT 300°C
- **BURNT, all**
  - MEAN OF ALL BURNT VALUES
- **pH smpl**
  - pH OF WATER SAMPLE
- **% SM ar**
  - % SOIL MOISTURE AFTER RAIN
- **% SM af**
  - % SOIL MOISTURE AFTER FLAMING
- **% OM**
  - % ORGANIC MATERIAL
- **COND**
  - CONDUCTIVITY m$^5$
- **COL**
  - COLOUR Ab/m
- **Fe**
  - IRON ppm
- **Al**
  - ALUMINIUM ppm
- **Mn**
  - MANGANESE ppm
- **Cl**
  - CHLORINE ppm
- **NO3**
  - NITRATES ppm
- **PO4**
  - PHOSPHATES ppm
- **SO4**
  - SULPHATES ppm
The above t-tests reveal no significant difference in colour between cores burnt at different temperatures and non burnt cores. Although mean colour values for core depths 5-10 cm do show greater levels of colour at all temperatures for burnt cores, the magnitude of these increases is not sufficient to be significant however, see Figs. 4.12 and 4.13.

THE EFFECT OF BURNING AT DIFFERENT TEMPERATURES ON SOIL MOISTURE, DIRECTLY AFTER BURNING

Table 3.9 and Fig. 4.11 show that burning has an effect on soil moisture at the surface of cores. T-tests indicate a significant difference in mean soil moisture between burnt and non-burnt cores, but no significant difference between cores burnt at different temperatures.

Significance (two tailed)

Soil moisture after burning

<table>
<thead>
<tr>
<th>Comparison</th>
<th>Significance</th>
</tr>
</thead>
<tbody>
<tr>
<td>B(300, 600, 800) vs NB</td>
<td>0.001</td>
</tr>
<tr>
<td>B300 vs NB</td>
<td>0.001</td>
</tr>
<tr>
<td>B600 vs NB</td>
<td>0.008</td>
</tr>
<tr>
<td>B800 vs NB</td>
<td>0.010</td>
</tr>
<tr>
<td>B300 vs B600</td>
<td>(0.103)</td>
</tr>
<tr>
<td>B300 vs B800</td>
<td>(0.523)</td>
</tr>
<tr>
<td>B600 vs B800</td>
<td>(0.490)</td>
</tr>
</tbody>
</table>

(       ) not significant.

SOIL MOISTURE VALUES AFTER LEACHING AND THEIR RELATIONSHIP TO COLOUR

Soil moisture values after leaching were measured to assess the ability of burnt cores to rewet. Table 3.9 and Fig.
3.31 indicate that their ability to rewet is unaffected by burning. Statistically, t-tests reveal no significant variation between burnt and non-burnt cores or between cores burnt at different temperatures, except those burnt at 300°C which showed a mean significantly different from all other groups. These results are thought unlikely to be due to the results of burning however, as they are not mirrored or amplified by burning at higher temperatures, rather they are thought to be a result of a lower starting soil moisture for the core as a whole, indicated in Fig. 4.11, and a lower organic matter content, affecting bulk density and in turn, apparent soil moisture, see Fig. 3.32.

RELATIONSHIP BETWEEN ORGANIC MATTER AND COLOUR
Measurement of percentage organic matter showed little variation between the cores burnt at different temperatures, see Table 3.9 and Fig. 3.32. Analysis of these measurements by T-tests revealed no significant variation in percentage organic matter for cores burnt at different temperatures with one exception, that of B300 vs B800 (signif at 0.087) shown in Fig. 3.32, this resulted from a lower mean organic matter value for the B300 cores, this was due to the presence of inorganic matter at the base of these cores rather than any effect caused by burning. The effect on organic matter at the surface of burning at 800°C , see Fig. 3.32, indicates that organic matter was lost through the burning of litter.
Fig. 3.31

% SOIL MOISTURE AFTER RAIN VARIATION WITH DEPTH AND TEMPERATURE OF BURNING (average of 3 cores per line).

Fig. 3.32

% ORGANIC MATTER VARIATION WITH DEPTH AND TEMPERATURE OF BURNING (average of 3 cores per line).
RELATIONSHIPS BETWEEN ALUMINIUM AND COLOUR

Regression analysis showed that aluminium was significantly related to colour for burned shaken samples. Regression equations being:

\[
    \text{Al (shaken)} = 0.0213 + (0.00711 \times \text{colour})
\]

\[
    \text{burned} \quad n=37, \quad r=0.750, \quad DW=1.84, \quad p<0.001
\]

Results for non-burned shaken and burned leached and shaken not being significant, although a general trend of increasing Al with increasing colour was apparent.

As expected, since there was no significant variation in colour between core groups T-tests showed few significant variations. Exceptions being for shaken samples,

- \( B(300, 600, 800) \) vs NB Signif. 0.054
- NB vs B300 Signif. 0.021
- B300 vs B800 Signif. 0.018

These variations matched the direction of the colour variations, but colour variations themselves were not significant, see Table 3.9.

The difference between leached and shaken samples produced unexpected results in terms of mean Al values, shaken samples produced less Al but more colour than leached
samples. The reason for this is unclear but may be connected with the stability of Al-organic acid compounds.

**RELATIONSHIP BETWEEN IRON AND COLOUR**

Iron values display significant positive correlations with colour, as expected;

\[
\text{Fe (leached) burned} = 0.0629 + (0.0151 \times \text{colour})
\]
\[n=31, \ r=0.680, \ DW=1.54, \ p<0.001\]
\[
\text{Fe (leached) non-burned} = 0.177 + (0.0118 \times \text{colour})
\]
\[n=11, \ r=0.560, \ DW=1.34, \ p<0.045\]

and

\[
\text{Fe (shaken) burned} = -0.144 + (0.0249 \times \text{colour})
\]
\[n=28, \ r=0.670, \ DW=2.03, \ p<0.001\]
\[
\text{Fe (shaken) non-burned} = -2.45 + (0.335 \times \text{colour})
\]
\[n=9, \ r=0.775, \ DW=2.67, \ p<0.005\]

(note the regression analyses for both the non-burned samples were carried out using a smaller sample population than would normally accepted by full statistical significance.)

T-tests revealed no significant variation, as with colour, the exception being the None Burnt Core (NB) vs Core Burnt at 600°C (B600) signif. at 0.061 (leached) the NB mean being higher than the B600 mean for Fe. This follows the same trend as colour, variation in colour not being significant however.
RELATIONSHIP BETWEEN MANGANESE AND COLOUR

Manganese was found not to be related to colour, as expected.

T-tests for shaken samples revealed no significant variation between groups, leached samples showed some significant variation,

\[
\begin{align*}
B(300, 600, 800) & \text{ vs } NB \quad \text{Signif. } 0.088 \\
NB & \text{ vs } B300 \quad \text{Signif. } 0.025 \\
NB & \text{ vs } B600 \quad \text{Signif. } 0.046 \\
300 & \text{ vs } 800 \quad \text{Signif. } 0.039 \\
600 & \text{ vs } 800 \quad \text{Signif. } 0.072
\end{align*}
\]

Variations appear to be random with respect to colour levels, following no set pattern, indicating why no relationship was found between colour and manganese.

RELATIONSHIPS BETWEEN NITRATE, PHOSPHATE, SULPHATE AND COLOUR

The regression equations did not show any significant relationship between these anions and colour, except the leaching values of SO₄ for burned cores, which indicated a positive correlation;

\[
SO_4 \text{ (leached)} = 33.44 + (2.43 \times \text{colour})
\]

burned \( n=31, r=0.50, DW=1.75, p<0.0262. \)
CONDUCTIVITY AND ITS RELATION TO COLOUR

Regression equations showed there was no significant correlation with colour. T-tests indicated a significant variation between NB and B600 for leached samples, a result attributed to natural variation as none of the other burnt core groups exhibited a similar variation. Conductivity would also be expected to increase after burning, not decrease, following the addition of ash.

RELATIONSHIPS BETWEEN SAMPLE pH AND SOIL pH WITH COLOUR

Mean sample pH and soil pH values are shown in Table 3.9 and Figs. 3.33 and 3.34 respectively. The regression equation for soil pH shows no significant relationship between colour and soil pH. T-tests for core groups on soil pH reveal no significant variation between groups, indicating that the potential addition of ash from burning has not altered the pH.

Regression analysis for colour versus sample pH similarly indicates no significant relationship.

T-tests for sample pH's show no significant variation except for B300 vs B600, such differences are explained by one high result at the surface of a core and another at the base, and are unlikely to be due to changes in ash content as these are not mirrored by other burnt cores or soil pH's.
Fig. 3.33

**SAMPLE pH VARIATION WITH DEPTH AND TEMPERATURE OF BURNING** (average of 3 cores per line).

![Graph showing pH variation with depth and temperature for burning (average of 3 cores per line).](image)

Fig. 3.34

**SOIL pH VARIATION WITH DEPTH AND TEMPERATURE OF BURNING** (average of 3 cores per line).

![Graph showing soil pH variation with depth and temperature for burning (average of 3 cores per line).](image)
3.1.3. CONSIDERATION OF DIFFERENCES IN MICROCLIMATE BETWEEN BURNT AND NON-BURNT AREAS

Observations suggested that the microclimate of burnt and non-burnt patches is substantially different over the summer months, the means of each variable are listed below:

<table>
<thead>
<tr>
<th>VARIABLES</th>
<th>BURNT</th>
<th>NON-BURNT</th>
</tr>
</thead>
<tbody>
<tr>
<td>Surface temp °C</td>
<td>23.90</td>
<td>16.38</td>
</tr>
<tr>
<td>Temp at 1cm°C</td>
<td>23.48</td>
<td>19.84</td>
</tr>
<tr>
<td>Temp at 2m°C</td>
<td>20.08</td>
<td>17.82</td>
</tr>
<tr>
<td>Incoming radiation</td>
<td>8.50</td>
<td>0.16</td>
</tr>
<tr>
<td>Outgoing radiation</td>
<td>0.94</td>
<td>0.16</td>
</tr>
<tr>
<td>Net radiation (surface)</td>
<td>19.75</td>
<td>1.83</td>
</tr>
<tr>
<td>Net radiation (2m)</td>
<td>18.90</td>
<td>13.68</td>
</tr>
<tr>
<td>Windspeed surface m/s</td>
<td>1.15</td>
<td>0.01</td>
</tr>
<tr>
<td>Windspeed (2m) m/s</td>
<td>3.60</td>
<td>3.90</td>
</tr>
<tr>
<td>Humidity (2m) %</td>
<td>53.65</td>
<td>56.62</td>
</tr>
<tr>
<td>Humidity surface %</td>
<td>49.42</td>
<td>68.41</td>
</tr>
</tbody>
</table>

Radiation measured in mv.
Non-burnt measurements taken under vegetation canopy.

Comparing soil temperature results for the non-burnt (vegetated) block 1 with the burnt block 3, suggest similar results, assuming the same pattern for other variables measured above the patches. Measurement of temperatures over the period 13.4.88 to 1.6.1989 showed significant differences between block 1 and 3.

Soil temperatures were measured at the surface and at depths of 1, 2, 3, 4, 5, 6 and 7cm. Mean differences at
each level are listed below with the results of the paired t-tests, significance level 90%, 0.10:

<table>
<thead>
<tr>
<th>Depth</th>
<th>Block 1 (NB)</th>
<th>Block 3 (B)</th>
<th>Signif.</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>S W S W</td>
<td>S W S W</td>
<td></td>
</tr>
<tr>
<td>Surface</td>
<td>12.31 2.71 14.81 2.80</td>
<td>0.000 (0.543)</td>
<td></td>
</tr>
<tr>
<td>1</td>
<td>11.27 2.72 12.38 2.97</td>
<td>0.002 (0.374)</td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>10.45 2.66 10.75 2.77</td>
<td>(0.180) (0.544)</td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>9.47 2.63 9.71 2.69</td>
<td>(0.238) not signif</td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>8.75 2.62 9.06 2.66</td>
<td>0.073 not signif</td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>8.37 2.62 8.65 2.69</td>
<td>0.029 not signif</td>
<td></td>
</tr>
<tr>
<td>6</td>
<td>8.33 2.62 8.49 2.68</td>
<td>(0.201) not signif</td>
<td></td>
</tr>
<tr>
<td></td>
<td>( ) not signif, S = Summer, W = Winter, N = 25.</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

These results are also clearly visible in figs. 3.35 - 3.39

3.1.4. SMALL SCALE STUDY OF THE SEVERE FIRE AT GLAISDALE.

Results from streams sampled are shown in Fig. 3.40 and indicate a wide variation in mean colour values between streams; as with Howstean, Inmoor and the Washburn, these differences can be related to catchment characteristics. Streams 1 - 6 produced little colour due to very thin organic soils, of these some catchments were not burnt whilst those that were burnt had been burnt at their head waters by the 1976 fire. Streams 7 - 15 mainly flow from burnt catchments, most having been burnt under management conditions producing a mosaic of burnt and non-burnt patches. Streams 17 - 21 are major streams flowing from the site of the severe fire of 1976.
Fig. 3.35

SURFACE TEMPERATURES FOR BURNT AND NONBURNT (CONTROL) BLOCKS (B3 & B1 respectively).

Fig. 3.36

TEMPERATURES AT 1cm BELOW SURFACE FOR BURNT AND NONBURNT (CONTROL) BLOCKS (B3 & B1 respectively).
Fig. 3.37

TEMPERATURES AT 2cm BELOW SURFACE FOR BURNT AND NONBURNT (CONTROL) BLOCKS (B3 & B1 respectively).

Fig. 3.48

TEMPERATURES AT 4cm BELOW SURFACE FOR BURNT AND NONBURNT (CONTROL) BLOCKS (B3 & B1 respectively).
Fig. 3.39

TEMPERATURES AT 6cm BELOW SURFACE FOR BURNT AND NONBURNT (CONTROL) BLOCKS (B3 & B1 respectively).

DATE

<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
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</tr>
</thead>
<tbody>
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<td>0</td>
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<td>0</td>
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<td>5</td>
<td>5</td>
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<td>10</td>
<td>10</td>
</tr>
<tr>
<td>15</td>
<td>15</td>
<td>15</td>
<td>15</td>
<td>15</td>
<td>15</td>
<td>15</td>
<td>15</td>
<td>15</td>
</tr>
<tr>
<td>20</td>
<td>20</td>
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<td>20</td>
<td>20</td>
<td>20</td>
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<tr>
<td>30</td>
<td>30</td>
<td>30</td>
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<td>30</td>
<td>30</td>
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</tr>
<tr>
<td>35</td>
<td>35</td>
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<td>35</td>
<td>35</td>
<td>35</td>
<td>35</td>
<td>35</td>
<td>35</td>
</tr>
</tbody>
</table>

Legend:
- B
- NB
3.2 THE EFFECT OF TERRESTRIAL LIMING ON COLOUR IN RAW WATERS.

3.2.0. SMALL SCALE LIMING EXPERIMENTS.

Examples of the results of colour levels and pH ranges obtained by differing doses are given in Fig. 3.41 to 3.46. Mean results are given in Table 3.10 for colour and Table 3.11 for pH.

Table 3.10 Colour (Abm⁻¹) Means for Shaking Experiments.

<table>
<thead>
<tr>
<th>Dose</th>
<th>PHAR</th>
<th>PHDW¹</th>
<th>PHDW²</th>
<th>WHAR</th>
<th>WHDW</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>8.7</td>
<td>16.3</td>
<td>44.11</td>
<td>19.14</td>
<td>40.64</td>
</tr>
<tr>
<td>1</td>
<td>19.20</td>
<td>28.66</td>
<td>------</td>
<td>23.62</td>
<td>35.80</td>
</tr>
<tr>
<td>2</td>
<td>29.98</td>
<td>30.14</td>
<td>57.72</td>
<td>30.9</td>
<td>47.32</td>
</tr>
<tr>
<td>4</td>
<td>25.60</td>
<td>31.94</td>
<td>39.56</td>
<td>33.08</td>
<td>44.24</td>
</tr>
<tr>
<td>6</td>
<td>20.70</td>
<td>27.04</td>
<td>28.5</td>
<td>43.06</td>
<td>38.50</td>
</tr>
<tr>
<td>8</td>
<td>18.02</td>
<td>20.46</td>
<td>7.75</td>
<td>35.58</td>
<td>34.40</td>
</tr>
<tr>
<td>10</td>
<td>15.02</td>
<td>17.06</td>
<td>4.80</td>
<td>33.88</td>
<td>23.10</td>
</tr>
</tbody>
</table>
Fig. 3.40

COLOUR AVERAGES +/- ONE STANDARD DEVIATION FOR NORTH YORKS MOORS STREAMS (Glaisdale).

- ave + SD
- ave Colour
- ave - SD

STREAM NUMBER
Table 3.11 pH Means for Shaking Experiments. Lime Doses 0 to 10 tonnes.

<table>
<thead>
<tr>
<th>Dose</th>
<th>PHAR</th>
<th>PHDW(^1)</th>
<th>PHDW(^2)</th>
<th>WHAR</th>
<th>WHDW</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>3.24</td>
<td>3.66</td>
<td>3.06</td>
<td>3.21</td>
<td>3.72</td>
</tr>
<tr>
<td>1</td>
<td>4.74</td>
<td>4.43</td>
<td>------</td>
<td>3.87</td>
<td>4.57</td>
</tr>
<tr>
<td>2</td>
<td>5.75</td>
<td>5.21</td>
<td>5.64</td>
<td>4.13</td>
<td>5.58</td>
</tr>
<tr>
<td>4</td>
<td>6.32</td>
<td>6.07</td>
<td>6.27</td>
<td>5.06</td>
<td>5.61</td>
</tr>
<tr>
<td>6</td>
<td>6.37</td>
<td>6.16</td>
<td>6.40</td>
<td>5.26</td>
<td>6.31</td>
</tr>
<tr>
<td>8</td>
<td>6.52</td>
<td>6.72</td>
<td>6.62</td>
<td>6.08</td>
<td>6.85</td>
</tr>
<tr>
<td>10</td>
<td>6.84</td>
<td>6.83</td>
<td>6.72</td>
<td>6.26</td>
<td>7.26</td>
</tr>
</tbody>
</table>

PH = Poorly humified, WH = Well humified, AR = Acid Rain, DW = Distilled Water

Whilst these results indicate that liming can change the levels of colour produced relative to unlimed samples, it cannot be said that increasing lime dosage necessarily produces increasing colour levels, nor is the converse true. At lower dosages, colour does increase but as the dose increases a point is reached at which colour levels begin to fall and continue to do so. Although the dosage at which this happens varies, colour levels in most cases do not approach those found in unlimed samples.
Fig. 3.42

Shaking Experiment: Colour from 8cm$^2$ dosed at 0, 1, 2, 4, 6, 8 & 10 tonnes. Shaken with 100ml of Chemical Rain, pH 3.8. Poorly Humified AR (PHAR).
Fig. 3.43

Shaking Experiment: pH of 8cm² dosed at 0, 2, 4, 6, 8 & 10 tonnes, shaken with 100ml Distilled Water, Poorly Humified DW (PHDWZ).
Fig. 3.44

Shaking Experiment: pH of 8cm$^2$ dosed at 0, 1, 2, 4, 6, 8 & 10 tonnes. Shaken with 100ml of Chemical Rain, pH 3.8.
Poorly Humified Peat Acid Rain (PHAR).
Fig. 3.45

Shaking Experiment: Colour from 8cm$^2$ dosed at 0, 1, 2, 4, 6, 8 & 10 tonnes. Shaken with 100ml of Chemical Rain, pH 3.8, Well Humified AR (WHAR).
Fig. 3.46

Shaking Experiment: pH of 8 cm$^2$ dosed at 0, 1, 2, 4, 6, 8 & 10 tonnes. Shaken with 100 ml of Chemical Rain, pH 3.8. Well Humified AR (WHAR).
### TABLE 3.12

**TABLE OF MEAN RESULTS FOR LABORATORY LIMED CORES.**

<table>
<thead>
<tr>
<th>LIME DOSE</th>
<th>% SM</th>
<th>% OM</th>
<th>pH soil</th>
<th>pH smpl</th>
<th>COND</th>
<th>COL</th>
<th>Fe</th>
<th>Al</th>
<th>Mn</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.00</td>
<td>82.42</td>
<td>92.43</td>
<td>2.25</td>
<td>3.20</td>
<td>151.67</td>
<td>40.04</td>
<td>1.0087</td>
<td>0.2695</td>
<td>0.0557</td>
</tr>
<tr>
<td>0.31</td>
<td>82.39</td>
<td>91.32</td>
<td>2.54</td>
<td>3.59</td>
<td>150.83</td>
<td>43.83</td>
<td>0.9645</td>
<td>0.3242</td>
<td>0.0896</td>
</tr>
<tr>
<td>0.93</td>
<td>81.95</td>
<td>90.34</td>
<td>2.89</td>
<td>3.49</td>
<td>157.14</td>
<td>33.51</td>
<td>0.9989</td>
<td>0.2457</td>
<td>0.0401</td>
</tr>
<tr>
<td>1.54</td>
<td>83.40</td>
<td>91.33</td>
<td>3.05</td>
<td>3.21</td>
<td>280.00</td>
<td>44.43</td>
<td>1.1900</td>
<td>0.3611</td>
<td>0.0307</td>
</tr>
<tr>
<td>LIMED, all</td>
<td>82.58</td>
<td>91.00</td>
<td>2.82</td>
<td>3.43</td>
<td>200.24</td>
<td>40.59</td>
<td>1.0573</td>
<td>0.3112</td>
<td>0.0621</td>
</tr>
</tbody>
</table>

**KEY**

- **LIME DOSE** in tonnes per hectare.
- **LIMED, all** MEAN OF ALL LIMED VALUES
- % SM, % SOIL MOISTURE
- % OM, % ORGANIC MATERIAL
- pH soil, pH OF SOIL
- pH smpl, pH OF WATER SAMPLE
- COND, CONDUCTIVITY $\mu$S
- COL, COLOUR Ab/m
- Fe, IRON ppm
- Al, ALUMINIUM ppm
- Mn, MANGANESE ppm
3.2.1. Large Scale Liming of Laboratory Cores at Differing Doses

Mean results for variables measured are given in Table 3.12.

Colour

Colour results with depth are given in Fig. 3.47, each line representing the average of three cores. Statistical t-tests reveal no significant difference between any combination of cores, combinations used for all tests being L vs NL (L=Limed, NL = non-Limed), 0 vs 0.31, 0 vs 0.9, 0 vs 1.3, 0.31 vs 0.93, 0.31 vs 1.5, and 0.93 vs 1.5, significance level 90%, 0.10.

pH

Results for pH with depth are given in Figs. 3.48 to 3.51 for both soil and water samples. Statistical t-tests revealed no significant difference between limed and non-limed cores for water sample pH for all groups. Soil pH showing a significant difference between L vs NL, significance at 0.013 (this being influenced by results for cores limed at 1.5 t/ha) and 0 vs 1.5 t/ha, significance at 0.10; all others showing no significant difference. As can be seen from Figs. 3.48 to 3.51 liming only affects the surface layers of the cores.
**Fig. 3.47**

**COLOUR (average of three cores) AT DIFFERENT DEPTHS FOR VARYING DOSES OF LIME (in tonnes per hectare).**

**Fig. 3.48**

**pH (SOIL & SAMPLE) VERSUS DEPTH FOR UNLIMED CORES.**
Fig. 3.49

**pH (SOIL & SAMPLE) VERSUS DEPTH FOR CORES LIMED AT 0.31 TONNES PER HECTARE.**

![Graph showing pH (SOIL & SAMPLE) versus depth for cores limed at 0.31 tonnes per hectare.](image)

Fig. 3.50

**pH (SOIL & SAMPLE) VERSUS DEPTH FOR CORES LIMED AT 0.93 TONNES PER HECTARE.**

![Graph showing pH (SOIL & SAMPLE) versus depth for cores limed at 0.93 tonnes per hectare.](image)
Fig. 3.51

**pH (SOIL & SAMPLE) VERSUS DEPTH FOR CORES LIMED AT 1.54 TONNES PER HECTARE.**

![Graph showing pH (SOIL & SAMPLE) versus depth for limed cores at 1.54 tonnes per hectare.](image)

Fig. 3.52

**IRON (average of three cores) AT DIFFERENT DEPTHS FOR VARYING DOSES OF LIME (in tonnes per hectare).**

![Graph showing iron (average of three cores) at different depths for varying doses of lime.](image)
IRON
Iron levels by depth are shown in Fig. 3.52, as with previous cores iron levels follow a similar pattern with depth, as colour varies, see Fig. 3.47. Iron is found to be positively correlated with colour, the regression line equalling:

limed \[ Fe = 0.281 + (0.0186 \times \text{colour}) \],
n=40, r=0.450, DW=1.21, p<0.001

unlimed \[ Fe = -0.218 + (0.0267 \times \text{colour}) \],
n=8, r=0.836, DW=2.03, p<0.002 (small population)

The lower degree of correlation for the limed equation indicates the additional effect on pH, the relationship between iron and colour normally being strongly correlated. Iron is, as expected, negatively correlated with the pH of the soil samples shown in Fig. 3.53, but whilst Fe levels decreased with increasing pH for water samples, the relationship was not significant.

T-tests revealed no significant differences between core groups.
SOIL pH VERSUS IRON FOR UNLIMED CORES AND FOR LIMED CORES

Regression line for limed (L) cores
Fe = 1.586 - (0.184 x Soil pH)
n = 41, r = 0.342, p < 0.026, DW = 1.59

Tops and bases of cores limed at 0.31 & 0.93 t.
ALUMINIUM

As with iron, aluminium follows a similar pattern to colour with depth, see Fig. 3.54. It is positively correlated with colour, regression equation equalling:

limed  \[ \text{Al} = 0.758 + (0.00740 \times \text{colour}), \]
\[ n=40, \ r=0.75, \ DW=1.76, \ p<0.010 \]
unlimed  \[ \text{Al} = 0.0430 + (0.00584 \times \text{colour}), \]
\[ n=10, \ r=0.760, \ DW=1.60, \ p<0.002 \]
(small population)

Aluminium is negatively correlated with pH, both for soil and water samples, see Figs. 3.55 and 3.56. T-tests showed no significant differences between core groups.

MANGANESE

For reasons to be discussed in Chapter 4, manganese is found not to be significantly related to colour. T-tests for core groups indicated no significant difference between cores.
Fig. 3.54

ALUMINIUM (average of three cores) AT DIFFERENT DEPTHS FOR VARYING DOSES OF LIME (in tonnes per hectare).

DEPTH (cm)

LITTER 0-5 5-10 10-15 15-20
SAMPLE pH VERSUS ALUMINIUM FOR UNLIMED CORES AND FOR LIMED CORES

Regression line for limed (L) cores
\[ Al = 0.670 - (0.104 \times \text{Water pH}) \]
\[ n=41, r=0.416, p<0.006, DW=2.36 \]

SOIL pH VERSUS ALUMINIUM FOR UNLIMED CORES AND FOR LIMED CORES

Regression line for limed (L) cores
\[ Al = 0.494 - (0.0636 \times \text{Soil pH}) \]
\[ n=41, r=0.471, p<0.002, DW=2.50 \]
CONDUCTIVITY
Mean conductivity rises gradually with increased doses of lime as might be expected, appreciable differences only become apparent at a dose of 1.6 t/ha. None of the t-tests indicated a significant difference. Conductivity is not found to be significantly related to colour.

ORGANIC MATTER AND SOIL MOISTURE
T-tests revealed no significant differences between groups, thus any large scale differences between groups in terms of the above variables are likely to be as a result of lime dosing rather than differing soil compositions. As previously established, colour values increase with organic matter content but no significant correlation is found though for this sample set as the actual range of values for organic matter is small, approximately 78-96%. The same is true for soil moisture, the range being 77.5 - 92.5%.

Note
Liming is also referred to in Section 3.3. and 4.0.3. as part of the Blocks Experiment in which a massive dose of lime was found to increase colour generation.
3.3. THE EFFECTS OF DITCHING ON COLOUR GENERATION AND ITS VARIATION WITHIN CATCHMENTS.

3.3.0. VARIATION OF COLOUR BETWEEN DITCHES

Sampling occurred for almost a year and indicated both spacial and temporal variation in colour. Figs. 3.57 and 3.58 show the nature of these variations, for a proportion of the year.

3.3.1. TUBE WELL SAMPLES AND WATER TABLE FLUCTUATIONS

Mean results are given in Figs. 3.59 - 3.61 along with the relative locations of tube wells and ditches.
Fig. 3.57

Fig. 3.59

Colour and Water Table variation at Howstean, run A.

Fig. 3.60

Colour and Water Table variation at Howstean, run B.
Fig. 3.61

Colour and Water Table variation at Gunnerside.
3.3.2. EFFECTS OF DRAINAGE ON SOIL MOISTURE

In all cases the mean moisture content of ditched peat (both in the blocks and the single ditched face) was lower than a control point situated in an untouched area of peat close to the experimental site (moor control), paired t-tests indicating a significant difference at <0.001. The isolated blocks, as expected, were significantly drier than the single ditched face of the moor, significant at <0.001 except for B1 which was significant at 0.008. Mean moisture levels for the above sites equal, 66.23% (moor control), 65.18% (B1 untreated), 64.64% (B2 droughted), 63.82% (B3 burnt), 64.55% (B4 limed), 65.17% (Single ditched face) given as the Moisture Fraction Volume (MFV) of the soil. An MFV of 1.0 equals 100% of volume of water, an MFV of 0.6 equals 60% water and 40% soil by volume.

3.3.3. BLOCK EXPERIMENTS.

pH levels in Block 4 rose almost immediately after liming, layers 1-4 equalling 6.5, 6.4, 6.3 and 5.8 respectively, whilst pH levels for the control (Block 1) equalled 3.9, 3.1, 3.4 and 3.6 respectively. Levels remained elevated through the sampling period.
Mean colour values for the burned, limed and control block are given below:

<table>
<thead>
<tr>
<th>Layer</th>
<th>B1</th>
<th>B3</th>
<th>B4</th>
</tr>
</thead>
<tbody>
<tr>
<td>LAYER 1</td>
<td>6.93</td>
<td>7.02</td>
<td>18.10</td>
</tr>
<tr>
<td>LAYER 2</td>
<td>25.31</td>
<td>21.14</td>
<td>19.04</td>
</tr>
<tr>
<td>LAYER 3</td>
<td>19.24</td>
<td>14.07</td>
<td>16.59</td>
</tr>
<tr>
<td>LAYER 4</td>
<td>13.85</td>
<td>19.67</td>
<td>33.23 Abm^{-1}</td>
</tr>
</tbody>
</table>

Colour results for each block per layer are given in Figs. 3.62 (B1), 3.63 (B3) and 3.64 (B4).

Mean results for aluminium and iron for the limed block compared to the control block are given below:

<table>
<thead>
<tr>
<th>Layer</th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
</tr>
</thead>
<tbody>
<tr>
<td>Aluminium</td>
<td>B4</td>
<td>1.400</td>
<td>1.287</td>
<td>1.247</td>
</tr>
<tr>
<td>ppm.</td>
<td>B1</td>
<td>0.296</td>
<td>0.421</td>
<td>0.340</td>
</tr>
<tr>
<td>Iron</td>
<td>B4</td>
<td>0.627</td>
<td>0.555</td>
<td>0.594</td>
</tr>
<tr>
<td>ppm.</td>
<td>B1</td>
<td>0.376</td>
<td>0.376</td>
<td>0.197</td>
</tr>
</tbody>
</table>
Fig. 3.62

Colour output from ditched untreated block, at layer 1. (b1L1).

![Graph showing true colour output from ditched untreated block at layer 1.](image)

Jan 1 1988 Jan 1 1989 Jan 1 1990

Colour output from ditched untreated block, at layer 2. (b1L2).

![Graph showing true colour output from ditched untreated block at layer 2.](image)

Jan 1 1988 Jan 1 1989 Jan 1 1990
Colour output from ditched untreated block, at layer 3. (b1L3).

Colour output from ditched untreated block, at layer 4. (b1L4).
Fig. 3.4

Colour output from ditched burnt block, at layer 1. (b3L1).

[Graph showing true colour output from ditched burnt block at layer 1.]

Colour output from ditched burnt block, at layer 2. (b3L2).

[Graph showing true colour output from ditched burnt block at layer 2.]
Colour output from ditched burnt block, at layer 3. (b3L3).

Colour output from ditched burnt block, at layer 4. (b3L4).
Colour output from limed burnt block, at layer 1. (b4L1).

Colour output from limed block, at layer 2. (b4L2).
Fig. 3.64

Colour output from ditched limed block, at layer 3. (b4L3).

Colour output from ditched limed block, at layer 4. (b4L4).
4.0. DISCUSSION OF RESULTS

4.0.0 CATCHMENT STUDIES.

These were designed to identify whether a pattern was identifiable between colour generation and catchment characteristics and the work has compared three catchments - Howstean (HS), Inmoor (IM) and Washburn (WB); their colour flows and the characteristics of their subcatchments. Results have shown that colour generation is not uniform even within catchments and therefore their specific characteristics are believed to account for the differences.

Colour varies both spatially and temporally in the HS, IM and W catchments and their values are displayed in Tables 3.1 and 3.2 and in Figs. 3.1 and 3.2.

ALL FOLLOWING COLOUR VALUES ARE EXPRESSED AS Abm⁻¹ AT 400nm.

Mean colour values were measured at subcatchment level and at HS they ranged from 2.87 (HS 3), to 12.29 (HS 14), averaging 6.48 for the catchment and IM exhibited a
similarly wide range, from 1.55 (IM 7), to 12.52 (IM 1), a catchment average of 5.58.

Water from these two catchments flows via the aqueduct which discharges into Scar House reservoir and it is noticeable that the average value of 4.84 of the mixed waters measured at this point, was similar to the calculated catchment averages for HS and IM combined. This similarity is expected because colour mix proportionally; any differences which do occur are as result of the varying volumes of water which flow from the subcatchments of different areas (McDonald, Naden, Martin and Mitchell 1987 - Water Authority Quarterly Report.)

Similar variations occur between subcatchments at the WB site, average values ranging from 2.60 (WB1) to 7.80 (WB11), the average for the catchment being 4.67. It is also apparent that this site generates much less colour than the HS and IM sites which is not unexpected given the known colour values at their respective treatment works.

The significance of the above subcatchment variations has been measured, using oneway analysis of variance, for all the catchments and confirms that a significant (p<0.01) variation exists between the subcatchments. Two of the HS subcatchments - 1 and 13 (HS2 and HS14), generate the two highest levels in the catchment. Differences are significant, between 1 (HS2) and subcatchments
2, 3, 4, 5, 11, 14 and 15; and between subcatchment 13 (HS14) and subcatchments 2, 3, 4, 5, 11, 12, 14 and 15.

At Inmoor subcatchments 16 (IM1), 18 (IM3), and 28 (IM 13) exhibit the higher colour values. Significant differences occur between 16 (IM1) and subcatchments 19, 20, 21, 22, 23, 24 and 26; and between subcatchment 18 (IM3) and subcatchments 19, 21, 22 and 23. Data available from subcatchment 28 (IM13) was unrepresentative because of extremely dry conditions which caused a much reduced inflow to the intake - and no outflow, this resulted in an artificial increase of colour level at this measuring location up to 75.00 Abm⁻¹. The inclusion of such high reading gave a mean value of 21.4 Abm⁻¹. (unadjusted), at which level there was significant difference from all other subcatchments, except 16, 17, 18 and 25. If however, these high values are removed and an adjusted mean of 8.59 Abm⁻¹. is produced, there is no significant variance from all other catchments. It is probable that the true mean lies between these two values and would show a similar significant variation to the unadjusted mean.

The highest colour levels at the WB site were observed in subcatchments 3, 4, 6, 8, 9 and 11; significant differences occurring between subcatchment 3 and 1; and subcatchment 11 and subcatchments 1, 2, 4, 7 and 10.
This evidence clearly indicates that spatial differences between levels of colour do occur between the subcatchments within a catchment. Temporal differences are also apparent, as indicated by the large standard deviations exhibited by colour data for individual subcatchments. Yorkshire Water Authority Data also supports the conclusion, see Figs. 1.1 to 1.4. As these significant variations were observed between and within catchments, which apparently were geographically similar, specific catchments and subcatchments characteristics were considered (see Section 2.4.0., for catchment descriptions.)

The relationship between the percentage area of deep peat within a subcatchment and the presence of colour, was closely examined and was found to be significant (p<0.002) using regression analysis for pooled data from the HS and IM catchments, (see Fig. 3.3). From this it is evident that the greatest amounts of colour come from subcatchments which are wholly or mainly covered by deep peat, (Winter Hill 1011b series). These areas have a huge potential to produce soluble organic matter, (discussed in Section 1.4.), as both humic and fulvic acid owing to their large areas and depths of mainly undecomposed plant material.

Despite this close relationship between deep peat and colour it is apparent that colour is generated in some HS and IM catchments which do not contain deep peat. This is explained by the type of soils (Wilcocks, Rivington,
Revidge and Belmont series) which these catchments contain; for, whilst these soils are not classified as peats, they all have peaty surface horizons and therefore the potential to produce humic and fulvic acids, although in significantly lower amounts than those generated in peat catchments.

Most of the significant variations in colour, observed in the HS and IM catchments closely follow the percentage area of deep peat which varies between 0.0% and 100.0%. The evidence for this relationship is as follows and it indicates the percentage area of deep peat, together with significant differences, from other subcatchments.

AT HOWSTEAN.

subcatchment 1 (HS2), (79.6%) differs significantly from: subcatchments 2 (0.0%); 4 (42.3%); 5 (0.0%); 11 (100%); 12 (67.1%); 14 (79.3%) and 15 (55.0%).

and subcatchment 13 (HS14), (100%) differs significantly from:

subcatchments 2, 4, 5, 11, 12, 14 and 15 (% as above) and 3 (1.3%)
AT INMOOR a similar pattern exists,
subcatchment 16 (IM1), (75.5%) differs significantly from:-
    subcatchments 19 (39.2%); 20 (5.4%); 21 to 24 and 26 (0.0%).

subcatchment 18 (IM3), (55.1%) differs significantly from:-
    subcatchments 19, 21, 22 and 23 (% as above) and 28 (46.0%).

and subcatchment 28 (IM13), (46.0%) differs significantly from:-
    all the others except 16 (75.5%); 17 (22.6%); 18 (955.1%); and 25 (4.8%), when the unadjusted figures are used.

However it is clear from the above that not all catchment differences can be explained by this relationship alone, exceptions for example are, HS streams 1 and 13 (HS 2 and HS 14) which generate much more colour than streams 8 and 9 (HS 10 and HS 11) have very similar amounts of peat, indicating that differences in colour generation are not attributable to quantities of peat alone.

At the Washburn site it is suggested that a similar relationship exists, the more highly coloured streams flow directly from moorland having deposits of peat, notably
stream 11 with approximately 75% deep peat, which differs significantly from subcatchments 1, 2, 4, 7 and 10. Subcatchments 2, 4 and 7 having no deep peat, 10 having a relatively small area of deep peat and subcatchment 1 being approximately 50% deep peat. Once again it is evident from streams 1 and 11 that not only pedology but other factors must be responsible for high colour flows, stream 1 having a mean colour value of 2.62 Abm⁻¹ whilst stream 11 has a value of 7.80 Abm⁻¹. Streams 3, 5, 6, 8 and 9 are also higher in colour than 1, 2, 4, 7 and 10 because these sampling points lie on the River Washburn between Thruscross and Fewston reservoirs; the coloured water coming from Thruscross in the form of compensation flow, Thruscross being mainly fed by stream 11.

This evidence, that the phenomenon of colour is not only a factor of pedological conditions, is reinforced by the comments in Section 1.0.2., which indicate that some Water Companies are unaffected by the problem of discoloration despite their having areas of peat deposits within their catchwater boundaries, see Fig. 4.1, (Smith, 1988).

In an attempt to explain the anomalies between pedology and colour production, anthropogenic factors were considered, burning and ditching being conspicuous at Howstean and Inmoor.
The relationship between colour and ditch length per unit area was found to be positive, regression analysis being significant at $p<0.15$, see Fig. 3.4. Although the significance would have been improved if more accurate ditch length/unit area data for Howstean Stream 13 (HS 14) had been available. This subcatchment has been densely ditched relatively recently (1984), compared to the other ditching phase at Howstean (1974) and this is probably responsible for the high levels of colour it generated, because of the additional ditching and the fact that high colour values cannot be explained only by the percentage of deep peat.

Field observations also show that in the remainder of the subcatchments the sides of the 1974 ditches have collapsed eroded and filled with peat and drainage impeded. Therefore water drained from these catchments less easily than from Howstean stream 13 (HS 14) where ditches are 'clean' and drainage is rapid, a factor which may influence the colour levels arising from these catchments.

The other anthropogenic factor examined was the practice of moorland burning in order to manage heather growth for Grouse as some of the catchments producing highly coloured flows were managed in this way. Although no significant relationship was found, it is suspected that one does exist as subcatchments which experience regular burning, generate high amounts of colour compared with non-burned peat.
catchments, having similar areas of peat. This may explain the variance in streams 1, 16, 18 and 28 (HS 2, IM 1, 3 and 13). For example, streams 1 and 16 have 79.6% and 75.5% deep peat and mean colours of 10.53 Abm⁻¹ and 12.52 Abm⁻¹ and are managed for Grouse, compared to stream 14 (HS 15) which has 79.3% deep peat and a mean colour of 5.0 Abm⁻¹ and is not managed for Grouse i.e. burnt. It is noted that catchment 11 on the Washburn is also burnt which may increase its colour generating capacity.

In addition to the foregoing anthropogenic factors it has been discovered that, between subcatchments, Fe, Al and Mn vary temporally and spatially with colour. Studies in the Washburn revealed variance significant at p<0.01 for Fe, p<0.01 for Al and p<0.01 for Mn.

For Iron (Fe) statistics reveal that stream 11 varies significantly from all other streams, a clear indication that Fe levels are related to upland peat catchments and colour. Regression analysis indicating that Fe is positively related to colour, significant at p<0.01.

The results for Aluminium (Al) were unexpected, as it has been proposed by the Water Authority that there was a positive relationship between colour and Al. In fact, for the WB site the relationship between Al and colour was found to be negative, significant at p<0.01. Analysis of variance indicating that stream 7 (no deep peat) with a
colour of 3.44 Abm\(^{-1}\) and mean Al value of 1.50 ppm. was significantly different from stream 10 (with deep peat) with a colour mean of 4.08 Abm\(^{-1}\) and a mean Al value of 0.48 ppm. The reasons for this are unclear, work described in Sections 4.0.1 to 4.0.3 indicates that there is a positive relationship between Al and colour, although even when relationships have been established, individual catchment characteristics may overshadow these relationships. It is possible that, because colour levels are relatively low, Al values from moorland flow are being overshadowed by those of the lower forested areas of the subcatchments. Nevertheless, it seems unusual that two such different patterns should emerge because Al and Fe are usually associated in both pedological and geological situations. Because of this enquiries were made regarding the forestry practices in these subcatchments, but no influencing factors emerged.

Manganese was found to be negatively related to colour, regression analysis significant at p<0.01, this result was similarly unexpected as a positive relationship had been previously proposed. Again this is thought to be caused by the influence of large values from lower forested areas of the subcatchments, values from streams 1 and 2 overshadowing those of 10 (4.08 Abm\(^{-1}\)), mean Mg 0.009 ppm and 11 (7.80 Abm\(^{-1}\)), mean Mg 0.08 ppm. Stream 1; mean colour 2.62 Abm\(^{-1}\), mean Mg 0.13 ppm, differing significantly from stream 9; mean colour 4.64 Abm\(^{-1}\), mean Mg 0.05 ppm and
stream 6; mean colour 5.22 Abm\(^{-1}\), mean Mg 0.05 ppm. Stream 2, mean colour 3.37 Abm\(^{-1}\), mean Mg 0.17 ppm, differing from all other catchments. However, such comments appear to be unjustified in the light of further work indicated in Sections 4.0.1 to 4.0.3 as Manganese is found not to be positively related to colour.

It was anticipated that the water sampling around Red Shaw Gill, Washburn Site, would provide an insight into the effects of clear felling, hence the large number of sampling points. However, the clear felling appears to have had little effect on colour production, stream 7 producing relatively little colour. This may be because the subcatchment concerned has not yet replaced the moisture deficit resulting from afforestation, thereby inhibiting colour from being leached in quantity from the soil. A further problem is that the other sampling points 5, 6, 8 and 9 are heavily influenced by the colour of the compensation flow from Thruscross reservoir, making it difficult to isolate any possible effects of clear felling. In addition, the pedology of the area concerned is the Rivington Soil Series (S41y), which does not contain large deposits of peat.

**RESUME OF RESULTS.**

The above results clearly indicate that colour varies spatially and temporally within subcatchments, the highest values originating in upland catchments which have a high
Fig. 4.1

Distribution of peat deposits in the British Isles (redrawn after Taylor, 1983)

Smith (1988).
percentage of deep peat, of the Winter Hill Series (1011b). In Fig. 4.1 (Smith, 1988) clearly shows the distribution of upland peat in the British Isles and indicates areas having the potential for colour production. As stated previously however, colour is not a country-wide phenomenon relating to peat areas for apparently similar catchments produce different levels of colour and by association, different levels of Fe, Al and Mn. This pattern, is also found on a subcatchment level at Howstean, Inmoor and the Washburn. It follows therefore that other factors are involved, demonstrated by the fact that subcatchments with similar quantities of deep peat have displayed significantly different colour values.

From catchment studies it is clear that the effects of burning (for Grouse management) and ditching, are potential producers of colour and in turn, high levels of Fe, Al and Mn. These anthropogenic factors are discussed further in Sections 4.0.1, and 4.0.3. The relationship between colour, Fe, Al and Mn is also addressed as the results for Al and Mn are opposite to those that were expected.

4.0.1 THE EFFECTS OF BURNING ON COLOUR GENERATION.

The results of small scale leaching and shaking experiments clearly show that there is a significant difference (leached \( p<0.01 \); shaken \( p<0.01 \)) between burnt and non-burnt cores, burnt cores producing more colour. Similarly,
burned cores produce greater levels of metal ions, Fe, Al and Mn, a significant relationship existing between colour and levels of Fe ($p<0.01$), Al ($p<0.01$) and Mn ($p<0.01$). These colour/metal ion relationships are not seen as being representative of field conditions however and as such the actual values are considered to be incidental. It is also apparent that the highest values of colour and metal ions are produced in the upper layers of cores, see tables 3.3 and 3.4.

Leached cores produced more colour than shaken cores, probably owing to the fact that they re-wet slowly and remain partially aerobic, possibly following the stages described by Birch (1958 a&b, 1959), whilst shaken cores were subjected to anaerobic conditions from the start of the experiment.

Leaching and shaking experiments also revealed the potential of small peat samples (25g), whether burnt or not, to produce large amounts of colour and metal ions at levels far in excess of the mean colour values found in subcatchment streams. For example, in the leaching experiments, the colour value means were 125.69 Ab$^{-1}$ for burned cores and 41.74 Ab$^{-1}$ for non-burned cores. Continuous leaching experiments indicated the same potential and showed that colour production was not a single event, rather it is a sustained process. Burned cores produced the greater amount of colour at first but
after a few days the non-burned cores were producing similar amounts, probably in response to the number of wetting and drying cycles and the warm conditions in the laboratory, see Figs. 3.6 to 3.9. This indicates that the problem of colour in supply is a long term phenomenon, as the potential for peat to generate colour is almost infinite under favourable conditions, peat being almost 100% organic matter.

Larger core experiments were more representative of field conditions both in terms of natural processes and the results obtained. From these results three tendencies in colour production are apparent: (i) Burned cores produce more colour than non-burned cores. (ii) Higher temperature burns (experienced under management) produce greater amounts of colour than low temperature burns. (iii) There is a time factor imposed on colour production, depending on fire characteristics and temporal variation depending on soil moisture deficits, determining when the colour is released.

These trends are shown in Figs. 4.2 to 4.5. Fig. 4.2 shows the average of the three cores for each group, burned Howstean (BHS), non-burned Howstean (NBHS), burned Inmoor (BIM) and non-burnt Inmoor (NBIM) for the April 1988 cores.
Fig. 4.2

COLOUR VARIATION WITH DEPTH FOR CORES TAKEN IN APRIL 1988.

Fig. 4.3

COLOUR VARIATION WITH DEPTH FOR CORES TAKEN IN AUGUST 1988.
Fig. 4.4

COLOUR VARIATION WITH DEPTH FOR CORES TAKEN IN JANUARY 1989.

Fig. 4.5

COLOUR VARIATION WITH DEPTH FOR CORE TAKEN IN APRIL 1989.
It is clear that one month after burning there is no difference between burnt (at low or high temperature) and non-burned cores. This suggests that the processes that lead to increased colour production in burnt cores are not a direct result of burning at management burn temperature. This factor that agrees with the work of Orioli and Curvetto (1978), which suggested that only soil temperatures over 250°C produce direct changes in humic fractions, soil temperatures in normal management burns not normally exceeding 100°C.

One possible direct effect of burning may be that of induced water repellency, although this does not directly produce colour. Work by Debano and Krammes (1966); Debano (1966); Cony and Morris (1968); Savage, Martin and Letey (1969); Savage et al (1972) and Savage (1974) has suggested that hydrophobic substances such as oils, waxes and resins, melt and migrate down the profile, forming organo-silicate complexes between translocated substances and soil particles. However, these chemical effects were only found to increase water repellency appreciably where burning had taken place at over 200°C, consequently it is unlikely that this is a significant factor in either of these management burns although the higher temperature burn may have reached such temperatures. Orioli and Curvetto (1978), do comment however that at normal burn temperatures partially burnt
organic residues generally result in more rapid mineralisation.

It is more likely that indirect effects are instrumental in colour production, requiring a length of time in order to alter soil processes sufficient to cause significantly large amounts of colour to be produced. These soil processes being related to decomposition and hydrological conditions.

Colour production was found to be relatively high for all cores, a phenomenon usually exhibited during the wetter months of the year when the products of decomposition are flushed out of the peat. A phenomenon evidenced by in Water Authority data which clearly shows seasonal fluctuations, see Fig. 1.1 (Thornton Moor).

By August 1988 burned Howstean (BHS), the high temperature burn, was producing significantly higher colour values than non-burned Howstean (NBHS) and both burned and non-burned Inmoor (BIM) and (NBIM); suggesting that the high temperature burn compounded the effects of burning on colour production, compared with those of the low temperature burn. The low temperature burn, BIM, not being significantly different from NBHS and NBIM. Three possible explanations exist to explain the differences between colour production in the high and low burn temperature cores, indicated by Fig. 4.3.
Firstly, that the low temperature burn has not affected the peat hydrology sufficiently to increase colour production, or that the effects have not had sufficient time to develop.

Secondly, that both BHS and BIM have been affected by burning but to different magnitudes; for example BHS may have been subjected to more frequent and more severe wetting and drying cycles, in its upper layers owing to the fact that the peat surface is largely bare and has a thin desiccation crust; whereas BIM was still largely covered by grasses, mosses and sedges so that any changes in hydrology are less severe. It is possible therefore, that BHS produced colour in amounts that saturated the exchange sites within the peat; consequently, excess colour molecules were leached via the soil solution; whilst BIM produced fewer colour molecules that could be held on exchange sites so that any increase in colour production was not transferred to the soil solution. Hence there is no apparent, significant difference between BIM and both NBHS and NBIM.

Thirdly, that the higher temperature burn has produced some additional effects on peat hydrology and in turn caused colour production to be increased at an earlier stage than in the low temperature burn.
Mean colour values, equalled BHS 31.40 Abm\(^{-1}\), BIM 7.23 Abm\(^{-1}\), NBHS 6.65 Abm\(^{-1}\) and NBIM 7.25 Abm\(^{-1}\) and for all cores were lower than those produced by the April 1988 cores. This effect was generated by the seasonal hydrology, less colour being generated, or released by leaching, in the drier, summer months.

By January 1989, shown in Fig. 4.4, it was clear that burning had affected both BHS and BIM, cores producing significantly higher colour values than for NBHS and NBIM. The high temperature (HS) burn is still producing more colour, mean 109.33 Abm\(^{-1}\) than the low temperature burn (BIM), mean 64.64 Abm\(^{-1}\). Colour means for non-burned cores equalling 34.89 Abm\(^{-1}\) for NBHS and 41.15 Abm\(^{-1}\) for NBIM.

It is apparent therefore that low temperature burning has affected peat hydrology and in turn, colour production; either because sufficient time has elapsed for an effect to take place; or colour production has exceeded the number of available exchange sites, causing colour to be leached out.

The greater amount of colour produced by BHS than by BIM suggests that either the magnitude and time scale of the effects of burning are greater and / or that other effects, for example the chemical alteration of HA and FA by increases in wetting and drying cycles has decreased the stability of organic matter, lowering its resistance to
microbial decomposition, (Raven and Avnimelech, 1978) leading to the production of greater amounts of colour.

In both cases the effects of burning are likely to have been compounded by the seasonal effect, linked with the autumn flush, the products of decomposition becoming hydrophillic and thus more readily leached from the cores. The so called "Birch Effect" (Birch, 1958 a&b) is also likely to have increased colour production, microbial populations expanding rapidly on rewetting. The autumn flush and the "Birch Effect" also affect colour production from non-burned cores.

Following the autumn flush of January 1989 (flushes occurring when the soil moisture deficit has been replenished, rather than at an exact time of year) colour levels from all cores decreased in April 1989, (BHS 52.42 Abm⁻¹, BIM 12.25 Abm⁻¹, NBHS 14.74 Abm⁻¹ and NBIM 9.22 Abm⁻¹), stores of colour having been depleted. However, the effects of burning on BHS are still evident, levels remaining significantly higher than BIM, NBHS and NBIM (p>0.002), but levels from BIM have become similar to those of NBHS and NBIM once again, see Fig. 4.5. This suggests that, either the effects of burning on hydrology are no longer present at the low temperature burn site, or that colour production was not currently high enough to exceed the number of exchange sites.
Colour production from all cores was lower than that for April 1988, a phenomenon most probably linked with the very dry conditions of April 1989, making cores difficult to rewet on leaching, slowing down decomposition and/or decomposition products becoming hydrophobic.

More detailed discussion of seasonal effects and the effects of wetting and drying cycles is given by Mitchell (1990) in his discussion of the 'natural' causes of colour generation.

Finally, general observations show that most colour is generated at a depth of 5-10 cm (for all cores) where microbial activity is at its highest in most soils. This observation and the work of Maltby (1980) North Yorkshire Moors (NYM), indicates greater bacterial numbers at this depth, especially on peat burned at management temperatures and the work of Birch (1958a) indicates that burning increases microbial numbers, leading to the generation of soluble colour. Colour flows, at depths > 5-10 cm, are affected by the availability of HA and FA acids and the amount of inorganic matter. As colour flows through the base of the cores, where the inorganic matter content is relatively high, it shows a reduction its level, HA and FA presumably being held on available exchange sites.
RELATIONSHIP BETWEEN COLOUR AND METAL IONS (Fe, Al & Mn).

Data collected in August 1988 and in April 1989 was used to examine the relationship between colour and metal ions. Analysis of the leachate from both burnt and non-burnt core sets, indicated that iron was significantly related to colour. The relationship for August 1988 being:

Burnt, \( \text{Iron} = 0.179 + (0.0144 \times \text{colour}) \) \( p<0.001 \);

Non-burnt, \( \text{Iron} = -0.0214 + (0.0490 \times \text{colour}) \) \( p<0.001 \);

and for April 1989;

Burnt, \( \text{Iron} = 0.0470 + (0.0178 \times \text{colour}) \) \( p<0.001 \);

Non-burnt, \( \text{Iron} = -0.211 + (0.0489 \times \text{colour}) \) \( p<0.001 \).

This is shown in Figs. 3.24 and 3.25 and it is apparent that anomalies do occur, for example, there are two high iron/low colour values in Fig. 3.24 which are explained by the fact that these samples came from the base of the cores, hence their low colour, having picked up iron in solution from the mineral content at these depths. A clearer relationship would have been obtained if colour and metal values had been divided into groups, related to depth and soil chemistry. However, this comparison would have been complicated by the fact that the leachate used had flowed from higher layers bringing inputs of iron and colour, which would have been exchanged or remained in solution, depending upon the soil chemistry of the next layer. This sequence and the fact that it is the relationship between colour and iron in surface waters, not within the soil profile, that is being examined; has
resulted in the data being considered as a single group rather than several groups. These comments also refer to the work done on Aluminium and Manganese.

These relationships are further supported by the fact that between cores, iron and colour show similar significant differences. Burned cores produce more iron than non-burned cores; high temperature burning produces more than low temperature burning. Both August 1988 and April 1989 cores from BHS produced significantly more iron than those from BIM, NBIM and NBHS (p<0.001 and p<0.019 respectively), following the same pattern as that of colour. In these two data sets the low temperature burn (BIM) does not show a significant difference in Fe levels from those of NBIM and NBHS, this is expected as the difference in colour levels, at these times, was not significant. From the established relationship between colour and iron it is postulated that the low temperature burn would have shown significantly higher levels of iron, if colour had been significantly higher as for example, in the January 1989 cores.

Iron is plotted against depth, for burned and non-burned cores, in Fig. 4.6. Comparison with Fig. 4.3 indicates, with a few exceptions, the similarity between the pattern of iron and colour generation.
Fig. 4.6

IRON VARIATION WITH DEPTH FOR CORES TAKEN IN AUGUST 1988. (Average of three cores per line.)
The strength of these relationships is not surprising as there is evidence that iron humate complexes are the real colour producers, Mitchell (1991). Ferric iron was found in natural waters at concentrations up to 100 times the theoretical value dictated by pH and redox potentials. An explanation being the relationship between iron and dissolved organic matter.

The relationship between aluminium and colour, using results from burned and non-burned cores was found to be less conclusive; no significant relationship was found for August 1988 cores, whilst for April 1989 burned cores \( \text{Al} = 0.140 + (0.00373 \times \text{colour}) \) \( p<0.001 \), and no significant relationship was found for non-burned cores, Fig. 3.26. Two points need to be considered about these relationships:

Firstly, the range of colour values for August 1988 is half that of April 1989 suggesting that if high colour values had been present, a significant positive correlation may have arisen, aluminium complexing with HA and FA. The chemical state of the measured aluminium is also important as the aluminium measured may be ionic or complexed with organic matter for if a large proportion of that measured in August 1988 is ionic, then a positive
correlation would be expected as colour levels rose and complexation occurred.

Secondly, the range of Al levels for August is higher than that of April despite mean colour values being greater in April than in August, a situation which appears to contradict that of a positive correlation. This contradiction is possibly explained by the fact that the two sets of results were measured by two different methods. Al results for August were measured using A.A.S. which may have given artificially high readings whilst the April results were measured by the more accurate I.C.P. method, although the relative chemical state of the aluminium is just as important which neither AAS nor ICP distinguish. Consequently, it is apparent that relationships arise only when relatively large colour values occur, April 1989, although the relationship is nowhere near as strong as that between iron and colour, as demonstrated by the comparison between burnt and non-burnt cores, few significant differences being found.

Figure 3.27 demonstrates the low level of variance in Al measurements between cores, indicating the reason why few of the statistical tests proved to be significant. It is evident from these results that burning at either temperature does not increase levels of Al in leachate,
either from August or April cores. Consideration should be
given however to the possibility that if colour values had
been higher, as in January 1989, a variation may have been
evident in view of the April 1989 regression equation.

A possible explanation of why aluminium forms a broader
relationship with colour than the close relationship
between iron and colour, is the relative stability of their
respective metal-organic complexes. Van Dijk (1971) states
that metal humic acid complexes involving iron are bound
more firmly than those involving aluminium, which tends to
form hydroxides, both soil and water complexation reactions
being strongly pH dependent, aluminium being leached from
the soil under acidic conditions, whether or not acidity is
generated by organic acids. Schnitzer and Hansen (1970),
demonstrated that the stability constants, expressed as log
K of metal FA-complexes, equal 6.1 for Fe$^{3+}$, 3.7 for Al$^{3+}$ and
2.1 for Mn$^{2+}$. Therefore, Fe > Al > Mn in terms of stability
for fulvic acid complexes.

Manganese was found to be negatively related to colour, for
April 1989 burnt cores p<0.03, Fig. 3.28, other results
producing a similar pattern but not at a significant level.
Manganese levels were found generally not to differ between
burned and non-burned cores a factor most likely arising
from the relationship between Mn and colour being a broad
one, low colour values displaying a wide range of Mn
values, possibly influenced by low colour, high Mn values,
from the base of cores and the low stability of Mn-organic complexes (as discussed above).

Differences between burnt and non-burnt cores are few, indicating that burning does not affect manganese levels. An effect if present however, would be likely to reduce levels of manganese rather then increase them.

RELATIONSHIP BETWEEN COLOUR AND NITRATE, PHOSPHATE AND SULPHATE.

Efforts to establish relationships between the products of decomposition and colour proved largely unsuccessful by this method, although T-tests reveal a pattern between colour and nitrate levels for April 1989 cores; BHS vs BIM and (BHS vs BIM, NBIM and NBHS), p<0.09 nitrate levels mirroring increases in colour levels. Phosphate was found to be positively correlated with colour p<0.017, T-test revealing significant differences between burned (notably BHS) and non-burned cores, burnt cores having high levels. Despite these results it is postulated that NO₃, SO₄ and PO₄ levels would increase with rising colour levels, as increasing levels of NO₃ have been recorded by Birch (1958a), Kreutzer et al. (1989), and Marschner et al. (1989) in response to increased microbial activity in peats (although increases in microbial activity were stimulated by liming, as apposed to burning).
The reasons for these results may be two fold; firstly NO$_3$, PO$_4$ and SO$_4$ are likely to form complexes with organic colour molecules (HA & FA) and SO$_4$ is likely to react with aluminium making these anions difficult to measure. Secondly the potential of these substances to be incorporated into HA and FA, means that only those substances remaining in ionic form will be measured by liquid chromatography, potentially giving much lower values for NO$_3$, PO$_4$ and SO$_4$. This effect is further exacerbated by the use of a guard column, which removes most HA and FA from samples, so that they do not poison the chromatography column used to measure anions.

Further work needs to be done therefore on the measurement of decomposition in burned and non-burned cores by using more direct methods, discussed later.

**RELATIONSHIP BETWEEN WATER SAMPLE pH AND COLOUR.**

No significant relationship was found between colour and the pH of the soil leachate, although the general trend within both data sets was towards a positive relationship, colour increasing as pH increases. These trends were misleading as the high colour, high pH, values were generated by very small volume samples which generated misleading pH readings. Although T-tests revealed little difference between burned and non-burned cores, indicating that burning did not increase the pH; there were exceptions.
These were explained by the two misleading small volume readings and by natural variations in NBIM, as it is clear, from looking at the mean values for the litter and those at 5 - 10cm deep in all cores, that burnt cores do not produce water samples of greater pH than non-burnt cores.

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Conversely, the mean pH for cores is affected by pH increases at the base of cores where inorganic matter is present in the soil profile, basic ions from carboniferous rocks increasing pH. This is indicated in Figs. 4.7 and 4.8, in comparison with organic matter Figs. 4.9 and 4.10.

It is clear therefore that burning has not directly affected colour merely by altering the pH of the soil solution, as increasing pH alters the chemical properties of HA and FA causing them to become more coloured. It also seems unlikely that soil pH is significantly affected by the addition of ash from burning, discussed in Section 4.0.2, as such effects would be expected to show in the pH of the soil leachate as peat is mostly water. Peat also has a large buffering capacity which will minimise any potential effect of ash on pH, therefore the increase of colour levels in burned cores is unlikely to be because of chemical alteration of HA and FA.
Fig. 4.7

**pH VARIATION WITH DEPTH FOR CORES TAKEN IN JANUARY 1989.** (Average of three cores per line.)

Fig. 4.8

**pH VARIATION WITH DEPTH FOR CORES TAKEN IN APRIL 1989.** (Average of three cores per line.)
Fig. 4.9

% ORGANIC MATTER VARIATION WITH DEPTH FOR CORES TAKEN IN APRIL 1988. (Average of three cores per line.)

![Graph showing the percentage of organic matter variation with depth for cores taken in April 1988, with lines for BIM, BHS, NBIM, and NBHS.](image)

Fig. 4.10

% ORGANIC MATTER VARIATION WITH DEPTH FOR CORES TAKEN IN APRIL 1989. (Average of three cores per line.)

![Graph showing the percentage of organic matter variation with depth for cores taken in April 1989, with lines for BIM, BHS, NBIM, and NBHS.](image)
Further, regression equations of pH against colour would normally be expected to be negatively correlated in the 'natural' environment, see Mitchell (1990), but positively correlated when considering the chemical properties of HA and FA, see Section 1.2.1. In the above cases no correlation is found because of the narrow range of pH between water samples, indicating that pH is not the causal factor increasing colour.

RELATIONSHIP BETWEEN CONDUCTIVITY AND COLOUR.
Water sample conductivity was measured to assess the effect of ash on the chemical properties of the peat by measuring potential increase in numbers of cations, but effects were found to be negligible as no significant differences were found between burned and non-burned cores and no relationships found between colour and conductivity. Other physical impacts of ash, for example in reducing infiltration capacity and stimulating biological activity, cannot be ruled out however (Mallik, Gimingham and Rahman 1984).

RELATIONSHIP BETWEEN COLOUR AND SOIL MOISTURE.
No significant relationship was found for April 1988, January 1989 and April 1989 cores, initial analysis suggested that colour was positively related to soil moisture, colour increasing as soil moisture increased, but consideration of the regression analysis showed that the regression equation in each case was unduly influenced by
just two low colour, low soil moisture, results which came from the bases of cores. Elimination of these two results led to the regressions becoming not significant. Similarly those T-tests which proved to be significant, indicating the same relationship, can be explained by low colour, low soil moisture values at the bases of cores, owing to differences in organic matter content, (c.f. Figs. 3.29 and 4.10) also see note 1 at the end of this section. Natural fluctuations also account for some of the significant differences, for example January 1989 cores, both burnt and non-burnt, from the same site reveal very little difference in soil moisture, differences only occur between site groups.

These results should be treated with caution however, they indicate that soil moisture is not affected on a long term basis by burning (at either temperature) and that increased colour generation is not a function of soil moisture.
It should be noted that these results only represent three isolated points in time and they do not take the following factors into account:–

i) The variations in soil moisture between burnt and non-burnt patches over the course of a year, which would allow for seasonal fluctuations and changes in microclimate.

ii) The precise form of moisture being measured.

and

iii) The time taken to produce hydrological effects and the length of time for which they remain.

The T-test results do show however, that the process of colour generation is not purely related to soil moisture at the time of leaching, but that other factors are involved, for example, the number of 'natural' wetting and drying cycles between leachings, Birch (1958a). Leaching removes stored colour within cores and/or rewets cores, initiating the process of colour generation, bringing colour into solution. These factors are discussed later in Section 4.1.0., as are the forms of moisture and the time taken to produce effects; annual variations in soil moisture owing to burning are discussed in Section 3.1.1. and in Section 4.0.3.
NOTE 1

The percentage of organic matter affects soil moisture readings, because as the proportion of inorganic matter increases, the bulk density of the soil increases, causing soil moisture to appear to decrease, whilst its actual volume may remain the same.

RELATIONSHIP BETWEEN COLOUR AND ORGANIC MATTER.

It is evident from the results from April 1988, 1989 and January 1989 cores that factors other than the percentage organic matter of the peat samples, are involved in the levels of colour production. Organic matter is, of course, an important source of organic acids, but differing colour values result from core samples of similar percentage organic matter, as shown in Fig. 3.30. This is emphasized by the fact that no significant relationship was found between colour and organic matter (OM), almost all the values falling in a narrow range between approximately 70% and 97% for organic matter, whilst colour ranges widely from 0 to 300 Abm⁻¹. Values which fall outside this OM range, for all core groups, represent the bases of cores where an inorganic component is present and relatively low colour values are recorded. Clearly had the range of OM values been wider and the number of low colour values greater, a positive relationship would probably have been found.
T-tests reveal a degree of variance between B and NB cores, but again these are mostly explained by increasing proportions of inorganic matter at the base of cores. Figs. 4.9 and 4.10 indicating that organic matter values in the upper parts of both sets of cores are very similar and as it is this part that produces most of the colour, see Figs. 3.8 to 3.23, it is evident that factors other than the percentage of organic matter are involved in its production.

The importance of the organic matter content would seem therefore to be secondary to other factors which influence colour production.

**EXPERIMENTS ON CORES BURNED IN THE LABORATORY.**

Results from cores burned at 300°C, 600°C and 800°C compared with non-burned cores reveal no significant difference in colour levels for either leached or shaken samples. This indicates that, as with cores from burnt patches in the field, the processes of increased colour production in burnt cores are not a direct result of burning, but rather of indirect effects which require time to produce significant differences in colour. Field patches burnt in March 1988, showed no significant difference when sampling occurred one month later, in April 1988, but significant
differences were apparent in August 1988. It seems unlikely therefore that at these temperatures and for short duration burns (1.5 to 2 minutes), representative of managed burns, that HA, FA and organic matter are directly affected chemically, producing yellow colour bands of low molecular weight and high mobility via the processes outlined by Oriolli and Curvetto (1978). These processes require soil temperatures greater than 250°C, which can only be obtained when all the moisture has been removed from the soil, normal managed burns do not normally exceed 100°C at 1cm depth, a fact supported by soil moisture values for burned cores directly after burning, Fig. 4.11. As Oriolli and Curvetto (1978) suggest, normal burning has indirect effects on the physical and chemical properties of soil humic substances over a period of time, suggesting that partially organic residues result in more rapid mineralisation. In view of this and with hindsight, it would have been preferable to have returned the cores to field conditions rather than to 'drought' them for the period of one month. This would have allowed 'normal' cycles of wetting and drying to occur, a factor that Birch (1958a) found to be very important in the production of colour.
fig 4.11
Fig. 4.11

% SOIL MOISTURE VARIATION WITH DEPTH AND TEMPERATURE OF BURNING (average of 3 cores per line).

![Graph showing soil moisture variation with depth and temperature of burning. The graph displays different lines for NB, 300°C, 600°C, and 800°C temperatures, indicating changes in soil moisture at various depths.]
Fig. 4.12

LEACHED COLOUR VARIATION WITH DEPTH AND TEMPERATURE OF BURNING (average of 3 cores per line).

![Graph showing leached colour variation with depth and temperature of burning.]

Fig. 4.13

SHAKEN COLOUR VARIATION WITH DEPTH AND TEMPERATURE OF BURNING (average of 3 cores per line).

![Graph showing shaken colour variation with depth and temperature of burning.]

Taking account of the above, Table 3.9 and Figs. 4.12 and 4.13 still indicate that the colour production from burned cores is potentially higher than that from non-burned cores, although not significantly so. It can be seen from Fig. 4.12 that at a depth of 5-10cm where colour is generally produced, burned cores generate more colour than non-burned cores, a factor thought to be related to microbial numbers. In these leached cores, those burnt at 300°C produced most colour at this depth, perhaps exhibiting their greater ability to rewet after drying, having been burnt at a lower temperature, thereby releasing stored colour or stimulating microbial activity. The cores burnt at 600 and 800°C exhibited less colour still but more than the non-burned cores and the indications are that they are more difficult to rewet after droughting and that the non-burned cores produce the least colour, owing to their high moisture levels compared with burned cores. As the moisture levels in the non-burned cores have stayed at the same level since they were collected, microbial activity has had no potential to increase, due to decreased soil moisture, during the month preceding the experiment. Microbial numbers are also less likely to increase when the cores are leached as there has been no cycle of drying and rewetting. (Colour produced by all the cores taken in July 1989 are similar to those produced by cores from August 1988 indicating the seasonal nature of colour generation,
i.e. lower levels being produced in the summer months, emphasising that burning has had little direct effect, over natural variations.)

Three theories of colour production are possible to explain this pattern:-

i) Soil moisture in cores burnt at 300°C has been reduced sufficiently to increase microbial activity, the upper parts of the core becoming aerobic. Soil moisture in cores burnt at 600 and 800°C becomes too low in their upper regions which either creates moisture conditions too adverse for the microbial population, or causes organic matter surfaces to become hydrophobic and thus difficult to decompose. Colour produced by this method is generated prior to leaching.

ii) Decomposition in the month prior to leaching is equal in the cores burnt at 300, 600 and 800°C but the ability to remove colour from the cores is affected by their rewetting capabilities, the core burnt at 300°C being able to rewet more easily, this allowing more organic acids to move into solution.

iii) Decomposition occurs on rewetting, in compliance with the 'Birch' theory that cores more able to rewet produce most colour, that is those burnt at 300°C rather than 600 or 800°C.
In light of the results of the shaking experiment of 5-10cm depth samples (see Fig. 4.13), theories ii) and iii) seem most credible as mean colour increases for all cores (including the NB core) on shaking. This suggests that the passage of colour into solution has been enhanced by agitation aiding rewetting. This is especially apparent as the shaken samples were much smaller (21.9g) than those in leaching pots which hold approximately 450g; yet mean colours for shaken samples exceeded those of leached samples! Samples from 600 and 800°C burns produced more colour at a depth of 5-10cm than non-burnt cores or cores burnt at 300°C.

The above theories are based on the experimental findings in association with related areas in the literature (Section 1.1), more research is required to establish the precise mechanism for increased colour production in burnt cores of different burning temperatures, it is apparent from naturally burnt cores, that cores burnt at higher temperatures produce more colour than those burnt at low temperatures. The potential processes responsible for such findings being discussed in Section 4.1.0.

THE EFFECTS OF BURNING AT DIFFERENT TEMPERATURES ON SOIL MOISTURE, DIRECTLY AFTER BURNING.

Burning was found to have little overall effect on the soil moisture levels within the cores burnt at 300°C, 600°C and 800°C. T-tests revealed significant differences only at
the surface of the cores when compared with non-burned cores, see Fig. 4.11.

These results were to be expected in the light of work by Oriolli and Curvetto (1978) and Hobbs and Gimingham (1984) who have recorded surface (0-1cm) temperatures of up to 100°C, sufficient to evaporate moisture, declining rapidly with depth to increases of only a few degrees centigrade at 5-10 cm, thereby having little effect on soil moisture. As can be seen in Fig. 4.11 the differences caused by burning only affect the surface layer of the cores between 0 - 1cm. Differences at 1cm, in cores burnt at both 300 and 600°C, fall within the natural range of moisture for all cores. Only the cores burnt at 800°C display a soil moisture lower than the natural range at 1cm. The differences in cores burnt at 800°C occur because moisture was largely removed from this layer, (readings at the surface equalling 8.57%, 5.00% and 11.20%) resulting in the thermal conductivity of the peat increasing to the extent that water at 1cm was partially removed by vaporisation.

Large differences in soil moisture do not occur, despite the large range of burning temperatures, because peat has a very low thermal conductivity due to its high moisture content. Therefore, if differences in burning temperature are to have a noticeable effect on soil moisture at depth, soil temperatures at the surface must increase to 100°C and be maintained for long enough to vaporise all the water
from the surface layer, before sufficient heat is transferred to the lower layers to reduce their soil moisture. Natural burning temperatures are not high enough or maintained for long enough for this to happen, normal burns pass over within 1 to 2 minutes. This was demonstrated by this experiment which was designed to simulate natural burning, temperatures ranging between 300 and 800°C and being maintained for between 1.5 and 2 minutes.

Regression equations of soil moisture versus colour for leached and shaken samples after burning, reveal no significant relationship, a result largely expected as colour values do not vary significantly, between cores. Had there been significant variation it would be expected that soil moisture would be negatively correlated with colour, drier cores producing more colour, assuming rewetting capacities were equal.

SOIL MOISTURE AFTER LEACHING AND ITS RELATIONSHIP TO COLOUR.
Statistical tests revealed no significant differences in soil moisture after leaching between burned and non-burned cores, clearly shown in Fig. 3.31.

These results are in accordance with those from cores 'naturally' burnt in the field, indicating that burning at these temperatures and durations has little or no permanent
effect on soil moisture conditions within the peat. The effects of fire induced water repellency (Debano and Krammes, 1966 and Savage et al., 1972 and other authors cited in Section 1.1.2.) appears negligible in both 'natural' and laboratory burnt cores. A factor to be expected in light of soil moisture results immediately after burning laboratory cores, these results indicated that soil temperatures are unlikely to have risen to 250°C, the level required to fix hydrophobic substances such as waxes and resins and impart water repellency. The fact that neither group displays a lower rewetting potential should be treated with caution for the effect on soil moisture may be more subtle than large scale differences in soil moisture. It may be only the soil water interface that is affected, large volumes of water being held in the peat structure but the surfaces of the organic matter remaining hydrophobic. These subtle changes may be caused by direct heating but for reasons discussed this seems unlikely, rather, hydrophobic surfaces may form as an indirect effect of burning, due to soil moisture fluctuations over a period of time. Drier conditions occurring owing to reduced infiltration capacity, Mallik, Gimingham and Rahman (1984); changes in microclimate, Whittaker and Gimingham (1962), Gimingham (1972) and Gimingham and Rahman, (1984); biologically induced water repellency, Maltby and Legg (1981); and the formation of crusts, Bridges (1986). Clearly these effects are unlikely to have affected burned laboratory cores, over the time
scale of the experiment, but they are thought to have been the influencing factors in the 'naturally' burned cores. The high temperature burn at Howstean exhibited desiccation crusts and markedly different microclimate (discussed later). These factors developing wetting and drying cycles (Birch 1958a) which probably led to the processes of increased colour production. These drying cycles may also affect the colloidal properties and stability of Humic compounds, Raven and Arnielech (1987), reducing their resistance to chemical and microbial decomposition.

To determine the relative importance and the precise nature of the above effects in terms of soil moisture, further work needs to be done on,

(i) the precise manner in which water is held in the soil;

and

(ii) the relative proportions of gravitational water and on the capillary and hydroscopic water (water which remains in the soil even after drying).

Soil water potential in combination with soil water content measurements should be used, allowing percentage moisture content to be related to the force in pF units at which moisture is held in the soil.
The suggestion that the above factors are important is further supported by the work of various authors, discussed in Section 1.1.2. under 'Fire induced water repellency' and in Section 1.1.3. under 'Biologically induced water repellency'; also by the fact that shaken samples release greater amounts of colour than leached samples (as discussed previously).

ORGANIC MATTER.
Further evidence in support of burning at management temperatures and durations not directly affecting peat cores is provided by the absence of any significant variation between percentage organic matter and core treatment, see Fig. 3.32. Burning did affect the surface percentage organic matter of the cores burned at 800°C, indicating that organic matter was lost through the burning of litter, temperatures being high enough to ignite litter and vaporise sufficient water. Even so, the effects are not large enough to affect mean organic matter values for the whole core and as such are seen as negligible, these effects being absent in cores burned at 300°C and 600°C. The fact that little organic matter is lost further supports the argument that fire induced water repellency is not significant in colour production at these temperatures, there being little volatilisation of humic substances. The similarity and narrow range of organic matter values also serves to emphasize that colour variations (leached and
shaken) are caused by soil processes rather than differences in soil composition.

RELATIONSHIPS BETWEEN METALS AND COLOUR.
Metal relationships were investigated as for 'naturally' burned cores, a similar pattern emerging, although precise relationships differ between sampling groups, dependent on soil chemistry and seasonal / burning effects. Aluminium levels were found to increase with colour levels, but only the relationship for burned, shaken cores was found to be significant p<0.001. All relationships between iron and colour were found to be significant, as expected; leached burned p<0.001, non-burned p<0.045; shaken burned p<0.001, shaken non-burned p<0.005; iron levels increasing with colour. No significant relationship existed between manganese and colour, T-tests indicating some significant variations in manganese levels but these are not consistent with increases or decreases in colour, suggesting that manganese levels are independent of colour levels.

RELATIONSHIP BETWEEN ANIONS AND COLOUR.
Attempts to relate nitrate, phosphate and sulphate to increased colour levels, as with measurements performed on samples from cores burned 'naturally' in the field proved unsuccessful. Only the relationship between colour and SO₄ for burned cores proving to be significant, p<0.002.
SO₄ values in leached samples revealed significantly more sulphate in samples from the non-burnt areas than from burnt cores. This suggests that sulphur may have been volatilised by burning, lowering the amount of sulphur (a product of anaerobic respiration) available to be oxidised. However, this possibility is not supported by shaking experiments or by results from field burnt cores. As commented previously, such work requires better methods of assessing potential increases in microbial activity and in turn colour production.

RELATIONSHIPS BETWEEN SAMPLE pH AND SOIL pH WITH COLOUR.
Relationships between colour and sample and soil pH were investigated to assess the effects of burning on pH, as pH is known to affect the chemical nature of humic and fulvic acids, increasing pH intensifying colour levels. The ranges of pH values both for soil and sample data, proved to be very narrow however, there being no significant differences attributable to burning, see Figs. 3.33 and 3.34. It seems unlikely therefore that burning would significantly alter pH by the addition of ash, and potentially chemically alter colour molecules. A fact supported by mean pH values at the surface of non-burned cores, being higher than those burned at 600°C and 800°C. Regression analysis revealed no significant relationships between colour and soil and sample pH. This suggests that colour differences between and within cores are not pH
related and that other processes are more likely to be influential.

It should be noted however that the effects of ash in these cores are likely to be minimal because surface vegetation was minimal compared with a 'natural' field burn. Nevertheless, it seems unlikely that the addition of ash will influence pH since no significant effect was observed in the pH of samples taken from cores taken from management burns in the field.

**OBSERVATION OF THE DIFFERENCES IN MICROCLIMATE BETWEEN BURNED AND NON-BURNED PATCHES.**

Results indicate that the potential for evaporation from the soil surface of the burned plot, is greater than that of the non-burned plot. Temperatures and radiation readings are higher over the burned plot leading to the more moisture being evaporated, higher wind speeds remove the evaporated moisture keeping humidity low which, in turn, promotes further evaporation. Even allowing for evapo-transpiration from the vegetation it is unlikely that the moisture loss from the non-burned plot would exceed that of the burned plot, as the albedo of the vegetation would be higher than that of the almost black surface of a burnt plot. For example, the albedo of grass, a crop similar to heather in colour and aerodynamic roughness, is about 25% (although this depends on age) whilst for burned patches, the mean albedo is 11%. Vegetation is also
capable of limiting evapotranspiration through the use of its stomatal pores, whereas evaporation from bare peat is purely dependent on the availability of soil moisture.

The dramatic effect that burning has on microclimate in terms of increased soil temperatures is apparent when comparing results from the vegetated block B1 and the burned block B3, clearly shown in Figs. 3.35 to 3.39. T-tests revealing significant differences for the surface $p<0.001$ and at 1 cm, $p<0.002$. The differences in temperature between the surface layers of blocks 1 and 3 being shown in Fig. 4.14. It is evident therefore that there is the potential for greater evaporation from the burnt block due to the greater amount of latent heat available, this potential is clearly seasonal however as marked differences in temperature do not occur in winter. Figs. 4.15 and 4.16 indicate the difference between the surface temperature of each block compared with air temperature, they clearly show the effect of decreased albedo in the burnt block, the nearly black surface absorbing more radiation than the vegetated surface, resulting in higher temperatures.

Similar changes in microclimate have been noted by Whittaker and Gimingham (1962) recording seasonal fluctuations in surface temperatures and increased evaporation from bare ground. Gimingham (1972) indicating that heather canopies reduce wind speed thereby reducing
TEMPERATURE DIFFERENCES BETWEEN BURNT AND NONBURNT BLOCK SURFACES (burnt hotter than nonburnt is +ve).
Fig. 4.15

AIR TEMPERATURE AND SURFACE TEMPERATURE FOR BURNT BLOCK.

Fig. 4.16

AIR TEMPERATURE AND SURFACE TEMPERATURE FOR NONBURNT BLOCK.
evaporation. Bridges (1986) also suggests that differences in microclimate enhance crust formation, this certainly seems to be true in the case of the Howstean burn of March 1988 (the burnt patch used for microclimate measurements), where a desiccation crust was seen to form. The magnitude of microclimate change is likely to be dependent on the characteristics of the burn. The Howstean burn had dramatic effects as shown by these results, whereas the Inmoor burnt area was likely to exhibit far fewer changes; because, for example surface vegetation was not completely removed, charred heather stems probably reduced wind speed, grasses and mosses protecting the surface from large temperature fluctuations and albedo remaining relatively high, there being no blackened charred surface. These differences potentially leading to lower moisture conditions and increased numbers of wetting and drying cycles at the Howstean burn, possibly explaining the greater production of colour compared with Inmoor.

Changes in microclimate may also lead to secondary affects, increases in surface temperature and decreases in soil moisture, leading to enhanced microbial activity, Bridgham et al., (1991), Imeson et al., (1988) and upon rewetting, the effects described by Birch (1958a&b). Increased frost heave, owing to high diurnal fluctuations, also exposes new surfaces to desiccation and microbial activity. These processes lead to the degradation of organic matter, and
produce HA and FA which passes into solution, generating colour.

**SMALL SCALE STUDY OF THE SEVERE FIRE AT GLAISDALE.**
This work produced unexpected results, in comparison to results from field burnt cores where higher burning temperatures were demonstrated to produce greater amounts of colour. The severely burnt site produced very little colour, whilst streams flowing from management burns produced similar amounts of colour to Howstean and Inmoor catchments that had been burnt, shown in Fig. 3.40. This seems to suggest that severe burning does not increase colour generation and may even suppress it.

Observations of the severely burnt moorland provided some suggestions for this pattern. The remaining peat layers were mostly thin with surface crusts (described by Bridges, 1976) and colonised by mosses and lichens, hardly any other revegetation being present. In places, the peat had actually been carbonized leaving a dry inorganic inert deposit. Descriptions of peat surfaces and their properties being given by Maltby (1990). Samples removed from the moor produced extremely low amounts of colour when shaken for several days with 'chemical' rain, suggesting little or no decomposition in these 'peats'. Stream samples were collected over the winter period at a time when colour values are usually at their highest, as these
were low it suggests that colour values are low all year round.

These observations and the work of other authors (Birch, 1958a; Debano, 1966 1969; Maltby, 1980; Savage, 1974;) suggest that severely burnt moorland is less likely to produce highly coloured flows owing to:

i) Chemical alteration of peats by extreme temperatures, rendering them hydrophobic and in some cases carbonizing them.

ii) The creation of water repellent layers or crusts, by both chemical and biological routes.

iii) The reduction of soil moisture to the extent that microbial activity is severely diminished or halted.

The above factors are considered further in Sections 1.1.2. and 1.1.3., the specific case of Glaisdale being discussed by Bridges (1986) and (Maltby 1980 & 1990).

As discussed previously, the above factors appear to be absent from normal management burns as temperatures are not high enough to produce such extreme conditions. Rather it is secondary effects on soil moisture, microclimate and microbial activity that are enhanced in such a manner as to increase colour production. Work done at Howstean and Inmoor and results from Glaisdale streams 7 - 15 support this, along with the work of Maltby (1980), peats burnt at
management temperatures exhibiting exceptionally large numbers of bacteria.

It is emphasized, that this study was only small and ideally, should be carried out over a longer period. Similar studies should also be extended to other sites as these studies only address the long term effects of severe fire on colour generation, the Glaisdale fire having occurred some 13 years earlier, both short term and direct effects need to be considered. Notwithstanding this, the severely burnt area does exhibit in places large quantities of desiccated peat, in the form of hags, which have the potential to generate colour but do not appear to influence / or produce colour in adjacent streams, suggesting that the processes which lead to colour production have been impaired, rather than that the supply of organic materials has been removed.

Further comments on burning are given in the section relating to the Block experiments.

RESUME OF RESULTS.

From the research on burning it is concluded that:-

i) Patches of burned peat moorland produce more colour than non-burned patches.
Under normal management burns, hotter fires lead to conditions that produce greater amounts of colour than do cooler fires; but severe fires, mostly accidental, do not increase colour production, and may even reduce it.

Strategies designed to limit colour production from heather burning are in accord with those good moorland management practices which maintain heather and may be summarized as the need to burn at optimum frequencies best suited to the age of the heather stands and within controlled areas. Management procedures designed to minimize colour production, do not adversely affect the important considerations of ecology, recreational needs and those of effective grouse management. To the contrary, they assist in each of these three areas.

Levels of Fe and Al increase with increased colour and therefore with burning. Levels of Mn being unrelated to these patterns.

4.0.2. THE EFFECTS OF LIMING ON COLOUR GENERATION.

From small scale experiments of shaking peat samples, both unlimed and limed at differing doses, with chemical rain or distilled water it is apparent that colour levels can both increase and decrease depending on lime dosage compared
with the levels displayed by unlimed samples. The five sample sets used are described as follows: one partially humified with acid rain (PHAR); two samples partially humified with distilled water, (PHDW') and (PHDW²); the forth well humified with acid rain (WHAR) and the last, well humified with distilled water (WHDW).

Only two sets indicated an overall reduction in colour. In PHDW² colour reduced progressively at dosages of more than 2 tonnes and in WHDW, colour decreased at dosages above 4 tonnes and continued to fall. Overall decreases in colour levels in these two samples was 89% for PHDW² and 43% for WHDW as compared with unlimed samples. Within these overall decreases however, PHDW² indicated a 31% colour increase at the 2 tonnes dose and in WHDW the increase was 16% at the same dosage.

In the other three sets a similar pattern emerged, colour again increasing with increased liming at the low to middle dosages, (2, 4 and 6 tonnes) and reaching maximum increases of 244% (PHAR), 49% (PHDW') and 124% (WHAR), all compared with the colour levels in the unlimed samples. At dosages beyond which these various colour maxima were reached, colour levels fall in each case but not as far as those of the unlimed samples, see Tables 3.10 and 3.11, Figs. 3.41 to 3.46. These indications that colour increases with relatively small dosing as humic substances become more soluble, accords with the work of Schnitzer and Kahn (1978)
and Tipping (1987) for the concentration of humic substances passing into solution increases as pH rises. Ultimate decreases in colour were not expected therefore, considering the effect of pH on the chemical properties of humic and fulvic acid, reviewed in Section 1.2.1.

Two potential causes present themselves:

(i) At a certain level of increase in pH the microbial population becomes inactive, or metabolism is slowed down, such that colour production ceases or becomes limited.

(ii) Colour complexes, notably those with Fe and Al are precipitated at higher pHs and thus colour is removed from solution.

Of these two potential causes, the second seems the more plausible due to the short duration time of the experiment and the anaerobic conditions.

The potential of metal-organo complexes to precipitate out of solution is commented on by Schnitzer and Hansen (1979) and Schnitzer and Khan (1978). When Fe$^{3+}$ and Al$^{3+}$ are added to humic substances at low pH, metal-organo complexes form, the solutions of which, when titrated with dilute base, form precipitates but these precipitates begin to dissolve as the titration proceeds and the pH rises above 7. The
stability constants of the complexes also increase with increasing pH. Thus, as pH rises, precipitates form and the filtered solution becomes less coloured, however, beyond pH7 one would expect colour to increase gradually as the precipitates dissolve again. However these comments conflict with those of Mitchell (1991) acidification causing the coprecipitation of humic substances with aluminium hydroxide, decreasing colour levels. Experimental results support the trend indicated by Mitchell (1991), but only up to a point, beyond which they differ. To a certain extent however, they also support the findings of Schnitzer and Khan (1978) as precipitation of colour occurred, but their work does not explain the initial increases in colour, at low liming rates. There is an indication therefore that further work on the precise chemistry of metal organic complexes relating to precipitation and solubilisation is required.

The pattern of changes in colour and pH are common between cores, but the dose at which colour peaks and falls, or the rate at which pH increases is soil sample dependent, a factor noted by Tipping (1987) and Christman and Gnassoni (1966). For the samples concerned colour begins to fall at the following mean pHs: PHAR = 5.75, PHDW1 = 6.07, PHDW2 = 5.66, WHAR = 5.24, WHDW = 5.60.

It should be noted that the proportion of lime to soil depth is large in this experiment, the dose per cm² being
equivalent to that spread in agriculture but only over a depth of 1 cm, whilst in reality peats can be up to 3 m or more deep. Thus, although effects of the above nature may take place at the surface of the soil, the experiment does not take into account the effects to the lower levels of the soil, or to the changes in the soil water as it flows through the lower layers. As soil water flows through the soil the 'lime' effect is greatest at the surface and diminishes with depth because of the relatively low solubility of calcite and the inhibiting effect of the peat structure on the movement of particles down the profile.

Large scale liming of laboratory cores at differing doses produced disappointing results, there being no significant difference in colour levels between limed cores at 0.31, 0.93 and 1.5 tonnes and unlimed cores which indicated that liming at these doses did not influence either colour production or the chemical intensity of colour. It can be seen from Fig. 3.47 and from examination of the raw data for pH (Fig. 3.51) that only the surface of the cores dosed at 1.5 tonnes shows any response to liming which, in all three cores, is not large enough to affect the mean for the whole core. Mean colour results for the surface of cores are respectively: 29.9, 34.16, 31.93 and 11.96 Ab/m for dosages of 0, 0.31, 0.93 and 1.5 t/ha. The colour reduction at the surface of the cores limed at 1.5 t/ha is surprising in view of the results produced by the small scale shaking experiments in which colour increased at this dose.
Equally, changes in sample water pH do not exceed 4.5 and thus are lower than those at which Fe and Al organo-complexes potentially precipitate out, reducing colour.

However, soil pH levels do exceed those at which Fe and Al organo-complexes potentially precipitate out and this may explain the reduction in colour, but this seems unlikely as dosing at 0.93 t/ha has a similar response affecting soil pH, but no reduction in colour. These results clearly show that liming at 0.31, 0.93 and 1.5 t/ha, comparable to levels used in maintenance dressings, does not decrease colour, the effect on pH being minimal, shown in Figs. 3.48 to 5.15. Sample pH indicated no difference between limed and non-limed cores, whilst soil pH only differed at a dose of 1.5 t/ha and even then, only at the surface, a factor related to the high buffering capacity of peat. This indicates that for liming to have an effect on colour, dose levels used need to be equivalent to remedial liming, at between 4 and 10 tonnes. Specific dose rates being determined by the precise soil chemistry of individual catchments and the need to increase the pH to more than 4.5, to create conditions favourable to the precipitation of metal-organic complexes. Following from the small shaking experiments however, which simulated liming at remedial levels, giving pH levels beyond 4.5, and indicating colour increase in most cases; colour reduction seems unlikely.
Metals were positively related to colour levels, as expected. Fe $p<0.001$ (limed) and $p<0.002$ (unlimed). Al $p<0.01$ (limed) and $p<0.002$ (unlimed). These metals were found to be negatively related to soil and sample pH as may be expected (Donald and Gee 1992, Diamond et al., 1992), iron and aluminium becoming less soluble as pH increases and colour presence being relatively low at these levels; but it can be seen in Figs. 3.53, 3.55 and 3.56 that the metal values, which influence the relationship as described, come from the tops of cores where liming has had an effect on pH and from the bases, where metal and pH levels are affected by inorganic matter. Therefore, liming has only affected metal levels (as with colour) in a small part of the core indicated by the fact that no significant differences were found for Fe and Al, between limed and unlimed cores.

It cannot be assumed however, that liming will reduce iron and aluminium levels in soil water for liming can potentially increase water colour by increasing the solubility of humic substances which have been shown to be related to Fe + Al, in the form of metal organo-complexes. As a result Fe + Al may increase in its organic form complexed to FA and HA, Adams and Evans (1989) and Kreutzer et al., (1989). Further research into the different forms of Fe + Al needs to be considered therefore in relation to organic acids and lime dosing.
Organic matter and soil moisture levels were measured in limed and unlimed cores; the fact that no significant differences emerged for these components indicates that they do not affect the above results.

RESUME OF RESULTS.

i) It has been shown that liming changes the levels of colour flow and that the levels of dosage affect these changes. Experiments have indicated that most and certainly heavy, applications do cause increased colour levels but that low dosages, when applied to peat cores, did not affect colour. At certain medium level dosages their ultimate effect was also to reduce colour levels after first increasing them, but not below those of unlimed peat. Consideration of the reviewed literature and experimental results leads to the conclusion that liming is not likely to reduce colour as humic substances become more soluble as pH increases. Whilst some literature suggests that colour is reduced by precipitation, given optimum pH conditions, this does not represent a 'true' decrease within the soil equilibrium, as only a chemical change has occurred which would be reversed if the soil acidity returned to its pre-liming level. Such a large and sudden release of colour would be in sharp contrast to the slower
release which takes place in naturally occurring acidic conditions.

ii) The amount of lime used and its subsequent effect on colour generation and solubility, is specifically related to the precise soil chemistry of individual peat samples, (the relationship between colour solubility and pH being soil specific). Therefore it is probable that in terms of soluble colour, individual catchments and their soils will exhibit different effects even after liming at the same dosage.

iii) Management strategy for reducing water colour by large scale dosing of lime does not appear to be a viable option as it is unclear as to the effect liming would produce on colour. Even if the correct levels of liming could be obtained to reduce colour it may be inappropriate, owing to; dosage being catchment specific; repeated applications being required; the potential to affect other water quality parameters; adverse affects on ecology and the problem of the reversible nature of the colour/associated metal ion reactions.

iv) Although liming of catchments has been shown to reduce levels of inorganic Fe and Al, the organic forms of Fe and Al may increase as a result of
liming, if colour increases. This results in the same water quality problems in terms of metal ions, only their chemical state is altered.

4.0.3. THE EFFECTS OF DITCHING ON COLOUR GENERATION.

The variation of colour between ditches showed a similar pattern to that between subcatchments within a catchment, indicating that variation occurs on a relatively small scale. Variations were both spatial and temporal, the colour ranged dramatically from visually colourless samples, to others which resembled weak tea and further to some which were almost black. Results are displayed in Figs. 3.57 and 3.58. Sampling clearly showed that colour levels from HS 14 are higher than those of NG, a factor related to the differing nature of soils within these areas. Ditches in both areas exhibited distinct types:

(i) Those that cut through the surface peat only, having peat sides and bases;

(ii) Those that had eroded beyond the peat layer into the subsoil, their bases being of sand and clay. Where ditches reached the edge of the plateau on the NG site bases consisted of the bedrock geology, the Yoredale Series;
In the case of the NG site several ditches produced consistently low colour values over the summer months, ditches usually being of type (ii) (hatched in Fig. 3.57). This indicated that the storage capacity of the peat was low and runoff rapid, due to relatively thin soils and diminished water tables, produced colour not being removed. Winter values showing increased colour as water tables rose and drainage gradients decreased, allowing colour to pass into solution. Type (i) ditches on thicker peat deposits displaying relatively higher colour values during the summer months than type (ii). This indicates slower response times and shallower drainage gradients thus allowing some of the products of colour generation to pass into solution. Seasonal increases in colour are still apparent however, as when water levels increase higher quantities of stored colour are flushed out.

Colour flows from HS14 were high, independent of ditch type, as the depth of the peat was sufficient to maintain water levels within the peat mass, allowing constant removal of colour from the large store within the peat. Small scale variations are still apparent however, most probably due to fluctuations in water levels and the thickness, chemistry and microbial populations of peat.

**Note**

Howsteane 14 (Stream 13) has two ages of ditching. A single Water Authority drain, which was originally dug to collect
and divert flow into the intake system and more recent ditching which was ploughed in 1984 to improve grazing and promote heather growth. Sampling points 1, 3, 5, 8, 11, 14, 16, 17, 18, 19, and 20 were situated on the main ditch. The remaining points represented inflowing ditches which connected with the main ditch. From Fig. 3.58 it can be seen how inflows from 1984 ditches affected the colour of the main ditch as it flowed towards the intake at point 1. The resulting colour being dependent on the volumes from each ditch.

Colour values from sampling points 17 and 19 were extremely high but very small in volume, hence the low range of values for sampling points down stream. These represent occasional flows from the eroding head of the main ditch, sampling points 18 and 20 being dry on the date these values were recorded. Such flows may have arisen from the re-wetting of desiccated peat at the ditch head or may be have been as a result of seepage from the deep peat, coloured by anaerobic processes over a long period of time. Whichever process is involved such values are surprising in the natural environment. It was also noted that on some occasions the apparent raw water colour was equally high at these points but upon filtration was almost colourless, (being less than 15 Abm⁻¹). This having been caused by colour precipitating out of the solution by some chemical reaction, possibly involving Fe and Al, however this matter was not further investigated.
The sampling of tubewell transects at Howstean and Gunnerside again showed a spatial variation of colour levels at a still smaller scale, shown in Figs. 3.59 and 3.60. Variations of water table depth are also indicated on these figures, indications are that drainage does not affect the water table as expected, following the work of Robinson and Newson (1986) and Coulson et al., (1990). Water levels were found to decline rapidly on either side of the ditches in both cases at Howstean and in one case at Gunnerside, although the remaining ditch there did show a depression in water table. These results were similar to those of Coulson et al., (1990), who found that the greatest depression in water table occurred immediately down gradient from the ditch in contrast to the studies of Robinson and Newson (1986) who observed sloping water tables from the midpoint between ditches to the ditch, water tables at both Howstean and Gunnerside fluctuated quite markedly between ditches, this pattern suggests that other drainage effects may have developed within the peat structure.

Water tables were found to decline substantially in summer at all points along the ditch transect and especially in tube wells adjacent to ditches, indicating that the surface layers of peat were aerated for long periods during the summer. This led to aerobic conditions which have been shown to increase microbial numbers and decomposition rates, Bridgham et al., (1991) and Coulson et
al. (1990) who has measured increases in decomposition rates of 70% in ditched catchments. The products of decomposition are flushed out during the water table rises in the Autumn; ditched Howstean catchments producing more highly coloured flows, especially HS 14, where these transects are situated, as discussed in the section on Large Scale Catchment Studies.

The precise effects on colour and water table fluctuations were shown to be ditch-dependent, runs A and B, being adjacent to each other, indicated that colour generation is dependent on localised soil chemistry, and on its structure and microbial populations as well as overall soil type.

Initially water levels were expected to be inversely related to colour levels. In some cases this broad relationship does seem to exist, but the processes of colour production and removal are too complex to follow this pattern closely, especially on such a small scale and given the relatively limited nature of the information.

Certainly colour stores within the peat are increased by the lowering of the water table, but the products of decomposition only pass into solution when water tables rise, flushing out the colour. Thus, high water tables can exhibit high colour levels. Equally, however, when the colour store has declined, high water levels will exhibit
lower colour values. Colour values are further dependent on anaerobic decomposition and wetting and drying cycles.

The numerous processes, coupled with the low hydraulic conductivity of peat, make deductions about colour values in relation to water table fluctuations difficult at this scale. The scale of variation within colour values, over such small distances, explains the differences in colour flows between ditches, for example, HS14 run A exhibits a lower range of colour values than that of HS14 run B, coupled with a lower range of water table depths. This suggests that colour production is indeed increased by the level of drawdown within the peat.

THE EFFECT OF DRAINAGE ON SOIL MOISTURE LEVELS.
The effects of drainage on peat were also apparent from the Block Experiments.

Mean moisture levels were as follows:

<table>
<thead>
<tr>
<th>Treatment</th>
<th>Moisture Level</th>
</tr>
</thead>
<tbody>
<tr>
<td>Moor control - unditched</td>
<td>66.23%</td>
</tr>
<tr>
<td>Block 1 - untreated control</td>
<td>64.64%</td>
</tr>
<tr>
<td>Block 2 - droughted</td>
<td>63.82%</td>
</tr>
<tr>
<td>Block 3 - burned</td>
<td>64.55%</td>
</tr>
<tr>
<td>Block 4 - limed</td>
<td>64.55%</td>
</tr>
<tr>
<td>Single ditched face of the moor</td>
<td>65.17%</td>
</tr>
</tbody>
</table>

(approximating to one side of a drainage ditch)

These readings appear to indicate that there has been little effect on soil moisture owing to ditching, the
values for the blocks and single ditched moor face being similar to that of the unditched sample point. However paired T-tests of soil moisture data over time indicate that the fluctuation between sampled groups is significant. Values for drained peat (both in the blocks and the single ditched face) were significantly lower than for undrained peat (the moor control), p<0.001. Similarly the isolated blocks had lower values when compared with the single ditched face of the moor, p<0.001. These results further demonstrate that ditching reduces soil moisture, allowing the upper layers of the peat to become aerobic.

Ditching is also likely to increase the number of wetting and drying cycles within the peat as water levels fluctuate, both effects led to increased microbial activity and increased decomposition, resulting in increased colour production.

It should also be noted that block 3 is significantly dryer than all the other blocks after burning, both at the surface and 10cm, this includes the droughted block, indicating that burning has had a dramatic effect on its soil moisture. The effect is limited to the surface layers though, explaining the lack of differences in the mean soil moistures quoted above. Differences between block 1 (control), block 2 (droughted) and block 3 (burned) are given in Figs. 4.17 and 4.18, clearly indicating that moisture levels are reduced in the surface layers, probably
Figure 4.17 Moisture changes in block surface peat
caused by changes in microclimate and infiltration capacity, a desiccation crust was evident on the surface.

**BLOCK EXPERIMENTS.**

Over the sample period colour results, for the control block (B1) and those treated to represent management practices (B3 and B4) are given in Figs. 3.62 (B1), 3.63 (B3 burnt) and 3.64 (B4 limed). From these figures initial high colour values can be observed in the early months after ditching. These values are thought to represent stored colour being released from the previously anaerobic peat as drainage occurred, a similar pattern being noted by Heathwaite, (1989 and 1991), in terms of nutrient release. Although such values may be a product of the autumn flush, but this seems unlikely however, as the majority of values are not repeated by the following years autumn flush.

Initial analysis of colour in layers within blocks revealed significant differences between treatments.

The burning of B3 produced no significant difference in layers 1 and 2 compared with the control (B1), layer 3 was found to be significantly less and layer 4, significantly more.

These results conflict with those of burned cores discussed in Section 3.1.1., where colour levels were found to increase in the upper layers of the cores. These results
may be attributable to excessive loss of moisture in the upper layers of the block through the effects of ditching combined with burning. The levels of colour generated having increased by the process outlined above in Section 4.1.0. but not being able to be removed from the block in solution, the rewetting capacity of the peat having been reduced to such an extent that organic matter surfaces have become hydrophobic. Similar patterns to those indicated above have been identified by McDonald et al., (1987), colour production being found to lag between three and fourteen months behind major droughts. It is postulated therefore, that upon rewetting, the surface layers of the block would produce significant amounts of colour.

The higher colour levels at layer 4 may be a result of increased decomposition due to burning, as the moisture levels were sufficient to remove colour in this layer, although this cannot be confirmed.

Block 4 revealed that liming had significantly increased colour levels in layer 1, 261% of the control value, in direct conflict to any suggestion that liming at high doses would reduce colour. The reasons for such increases are discussed in Section 4.1.1. It is clear from Fig. 3.64 and the mean values of colour that significant increases are restricted to layer 1, despite the fact that the 'lime' effect seemed to be present throughout the layers of the block indicated by the pH values of the water samples which
were taken. This seems to suggest that increases in colour may be due primarily to the improved microbial conditions due to ditching and liming rather than to the chemical effects on FA and HA.

Chemical effects would be expected to increase colour levels throughout the block as pH increases are exhibited in leachate from all layers. However, the pH response appears to be more likely, as in the control block, colour levels have not increased to a similar level to those at the surface despite the improved microbial conditions. This suggests that either liming has a profound effect on microbial activity compared with that of ditching or, that a combination of processes are at work. The levels of soil pH may also be a factor instrumental in colour production, but as shown in the core experiments, it is only likely to be increased at the surface.

Colour values at layer 4 were 240% of that of the control and significantly different to those of other blocks; due to the very wet conditions around the base of this block having increased the wetting and drying cycles; or, due to high values resulting from the anaerobic conditions coupled with high residence times; or due to the effect of high pH leachate mixing with the waters of this layer. In fact, all three conditions may have caused the maintenance of high colour levels.
The results of metal ions Fe and Al measured in the leachate from Block 4 were unexpectedly high as liming usually reduces their levels, increases in pH decreasing their solubility.

As discussed in Section 1.2.1. these increases are thought to be due to Fe and Al forming complexes with organic acids thus being removed from the peat in solution.

RESUME OF RESULTS.

i) Flows of colour from individual ditches vary from catchment to catchment depending on soil type and ditch type. Within single sub-catchments, where soil represents a constant variable, large fluctuations in colour are apparent, suggesting that other variable factors are present, notably water table depths. (Although differences in precise soil chemistry cannot be ruled out). Colour flows from ditches exhibit seasonal variations.

ii) Drainage is seen to have an effect on water table levels, evidence of drawdown occurring alongside ditches. The height of the water table also fluctuates between ditches which indicates the presence of other forms of enhanced drainage, possibly as a result of accelerated flows due to ditching. Colour flows also fluctuate with the
height of the water table but no clear relationship exists at this scale, due to the complex nature of the production and removal of colour and to the low hydraulic conductivity of peat. The above effects are not instantaneous, there is a lag between drying out and the production of colour. There is also a lag between rewetting and the removal of colour in solution. The duration of these time lags are both dependant upon the precise levels of stored colour and soil moisture conditions.

iii) It is clear from the drainage of the experimental blocks of peat and single faced cuts, that drainage depletes soil moisture. It can be inferred then, that this increases colour owing to the processes previously discussed. The precise relationship between moisture and colour production (for the drained block peats) is still being assessed.

4.1. CONSIDERATION OF THE PROCESSES LEADING TO CHANGES IN COLOUR PRODUCTION AS A RESULT OF BURNING, LIMING AND DITCHING.

This section is designed to identify the probable processes and factors that influence colour production due to burning, liming and ditching and is compiled from the literature discussed in Chapter 1 and from the results of this research. Although further work is required to
identify the exact mechanisms involved. Discussion is brief as the processes of colour generation were not the primary objective of this research. Specific processes in terms of moisture relationships and microbial activity being addressed by Mitchell (1990).

4.1.0. PROCESSES LEADING TO INCREASED COLOUR PRODUCTION FROM MOORLAND SUBJECTED TO BURNING.

The probable processes of increased colour production are all linked to the establishment of drier conditions within peat soils, allowing aeration to occur and in turn, decomposition to increase, resulting in the release of organic acids and leading to water discoloration. The process involved being displayed in Fig. 4.19.

Research suggests that under normal management burns, at temperatures commonly between 250°C and 600°C (depending on the age of the vegetation stand), colour production increases with temperature above that of unburnt moorland. Colour production is not instantaneous and thus not a direct result of burning but rather that several indirect effects increase colour production over time. Such effects seem to be those listed under the provisional effects on soil moisture, as gross measurements of soil moisture reveal that peat is not permanently affected by burning at these temperatures, a factor displayed by comparing field burnt cores with laboratory burnt cores (previous comments
on capillary and hydrosopic should be taken into account). It seems unlikely that colour production is affected by pH increases arising from ash, as pH in both water and soil samples does not vary appreciably between burnt and non-burnt cores. It is therefore most unlikely that the increase of colour is caused by the chemical alteration of humic and fulvic acids but ash deposits may enhance microbial activity, by increasing the level of available nutrients.

It seems that soil moisture is affected by the results of burning on the microclimate, which dries the upper layers of the soil profile sufficiently to destabilise organic matter, thereby increasing the number of surfaces open to microbial attack. Decomposition is enhanced by aerobic conditions, increased soil temperatures and improved nutrient status. Changes in microclimate would also increase the number of wetting and drying cycles, thereby increasing decomposition due to the Birch (1958ab) effect. The products of decomposition are removed in the autumn/winter season as throughflow increases, flushing out organic acids in the form of discoloured water.

As these effects, are mainly physical and biological they last as long as bare ground is dominant and as revegetation progresses these processes are likely to be reversed, leading to lower productions of colour. This potentially explains why the increased colour levels at the Inmoor, low
temperature, burn site, returned to levels exhibited by non-burned sites 1 year after burning, as apposed to the high temperature burn at Howstean, which still exhibited significantly higher colour values over non-burned sites. The Inmoor site having little bare ground, whereas the Howstean site was still largely bare, revegetation being reliant on germination from seed. As the age of the canopy and in turn the temperature of the burn affects the speed of revegetation, older, hotter burns are likely to be exposed to drier conditions for longer periods than younger cooler burns. Revegetation is relatively rapid after burning from late building phase stands, whilst mature/degenerate stands require longer periods. Differences in levels of colour production, from different temperatures of burns, probably is due to the fact that hotter fires completely remove all vegetation from surfaces, including mosses and grasses, increasing the effect on microclimate and altering FA and HA chemically, so that organic acid molecules become easier to decompose.

Following severe fires however, there appears to be permanent effects on soil moisture, colour production being reduced or equal to that of non-burnt areas, Fig. 4.19. Peats forming crusts, which are water repellant layers, and organic molecules become completely hydrophobic and unable to rewet. Consequently microbial attack is minimal, due to the unsuitability of the substrate and dry conditions. The
duration of such effects is unclear, but such effects are present at Glaisdale, thirteen years after the fire.
Fig. 4.13 Potential Processes for Colour Production on Burnt Moorland.

**Evaporation**

- **VEGETATION** → **REMOVED**
  - Low temp
  - High temp
  - PARTICULARLY WHOLLY

- **BURNING** → **SOIL MOISTURE**
  - Temps reached, age of heather, soil moisture conditions
  - Long duration severe fires 800-1000°C
  - Short duration management burns 250-600°C

**Microclimate**

- **
  - >ALBEDO
  - >WINDSPEED
  - >LATENT HEAT
  - >HUMIDITY
  - >SOIL TEMPS

**Revegetation**

- Swift 1-2 seasons
- Grasping pressure Slow 2-8 management burn
- Forested

**Effects**

- Short term
- Long term or permanent

**Colour**

- Effect = Chemistry of FA + HA acids
- Leaches out = pH
- More colour = More colour
- Less or no colour = Poorer soil conditions
- Complexation = Fe, Al, Mn

**Decomposition**

- >No of NUTRIENTS
- >No of WETTING and DRYING CYCLES
- INCREASED BETTER SOIL CONDITIONS
- Decrease = Drying
- Increase = Drying
- Stabilizes = FA + HA decreases
- Organic molecules unavailable = Throughflow

**Ash**

- Chemical, biological, and hydrological
- Ash

**Infiltration**

- Chemical, biological, and hydrological
- Biological, hydrological

**Crusts/Water Repellency**

- Chemical, biological, and hydrological
- Chemical, biological, and hydrological

**Water Repellency**

- Chemical, biological, and hydrological
- Chemical, biological, and hydrological

**Effects Short Term**

- Effects Long Term or Permanent

**Better Soil Conditions**

- Anaerobic at base of soil profile
4.1.1 PROCESSES LEADING TO INCREASED COLOUR PRODUCTION AS A RESULT OF LIMING.

Potential processes and areas requiring further research are presented in Fig. 4.20.

It is apparent from the literature that humic substances become more soluble and that colour intensifies chemically, as pH increases. Experimental results are in accordance with this pattern, liming at maintenance and remedial levels increases colour. No evidence has been found during this research that colour is precipitated by the formation of metal organo-complexes with Al and Fe, to the extent that colour is reduced below that of unlimed peat. If however, liming was to achieve colour reduction by precipitation it should be noted that this reaction is reversible upon acidification, which would release greater quantities of stored metals and humic substances, Marschner et al., (1989). Colour levels potentially following the curves shown in Figs. 3.41, 3.42 and 3.45, reading from right to left. The above only considers the chemical processes linked to liming, it is apparent that other indirect effects may further enhance colour production, noted in the literature. In particular, amelioration of
Potential Processes Involved in colour Reduction/Increase due to Lime Dosing.

**ACID RAIN**

![Diagram showing potential processes involved in colour reduction/increase due to lime dosing.](image_url)
acidity may enhance microbial decomposition, Bridgham et al., (1991), Maltby (1979 and 1984) and Abrahamsen et al., (1980), leading to increased colour levels, either stored as precipitates or in solution. This means that if liming is to be considered as an option for reducing colour there are many further questions which must be answered, for example:- (1) the effect on microbial activity and populations (particularly actinomycetes); (2) the effect on the solubility of FA and HA with regard to Fe; (3) Al organo-complexes and their potential to precipitate with dilute bases and (4) the precise soil chemistry for individual catchment soils to assess the dose of lime required to raise pH such that organic acids precipitate out in association with metals.

4.1.2 PROCESSES LEADING TO INCREASED COLOUR PRODUCTION AS A RESULT OF DITCHING MOORLAND.

The potential processes of increased colour production due to ditching are summarized in Fig. 4.21. As mentioned previously, ditching initiates similar processes to those of burning and (to some extent) liming; as such, once soil moisture deficits have been produced, colour production follows a similar path, despite the nature of the management practise responsible for soil moisture modifications. Liming is only partially similar because moisture fluctuations are not involved. However, the processes of decreased stability of FA and HA and the
Fig. 4.21

Potential Processes Involved in Colour Increase due to Ditching.

REASONS FOR, Forestry, Pasture Improvement (lime dosing), Regeneration of heather (burning)

DRAINAGE

Density, depth, soft or hard ploughing topography

FORESTRY + BURNING
> effects of

SEDIMENT TRANSPORT

Increased

EROSION. DOWN CUTTING. REMOVAL OF PEAT IN DRAINS over time can reach inorganic subsoil

STABILITY of FA + HA decreases

(HYDROPHOBIC FA + HA)

RAINFALL

WATER TABLE DRAWN DOWN. Dependant on depth of drain, thickness of peat, hydraulic conductivity

< SOIL MOISTURE

AERATION

WATER TABLE FLUCTUATIONS

BETWEEN PEAT LAYERS, LOW COLOUR FLOW (summer)

WITHIN PEAT LAYERS, WET UP COLOUR (winter)

< WETTING + DRYING OF PEAT

INCREASED MICROBIAL ACTIVITY

> DURATION OF SUMMER FLOWS

> SOIL MOISTURE DEFICIT

AEROBIC SOIL CONDITIONS

INITAL REMOVAL OF HIGHLY COLOURED WATER FROM PEAT produced by anaerobic conditions combined with low hydraulic conductivity = high residence times

(Clear felling > height of water table flushing out FA + HA)

> Fe + Al

Al, Fe, Mn Complexation

FA + HA Production of DECOMPOSITION
increased microbial activity, are still initiated, although by a different route.

The effects of drainage are likely to vary depending on several factors:

(i) The type of ploughing/ditching being either 'hard' or 'soft';

(ii) The density of the ditching;

(iii) The degree of drawdown produced. This being dependent on (i) and (ii), as well as the depth of peat and the degree of erosion and sediment removal;

(iv) The land use after ditching. Forestry for example may further increase the level of drawdown through increased interception (38%) and transpiration (12%) of gross precipitation, run off being reduced to 50%. Further, water tables increase after felling as evaporative losses decrease and result in an increased run off up to 68%, Anderson et al., (1990). This process probably leads to increased decomposition during the years of afforestation, followed by removal of colour upon felling. Grouse management and/or pasture improvement, may exacerbate the processes of colour production, by burning and/or liming.

Block experiments also revealed that the drainage of blanket bogs releases initial amounts of highly coloured water from the store of colour within the bog, this
presumably being produced by anaerobic decomposition over a long period.

4.2 RECOMMENDATIONS FOR THE MANAGEMENT OF MOORLANDS BY BURNING AND DITCHING. THE RESPONSE TO THE PROPOSAL THAT COLOUR MAY BE MANAGED BY APPLICATION OF LARGE DOSES OF LIME.

4.2.0. CATCH WATER MANAGEMENT RECOMMENDATIONS.

Results from Howstean, Inmoor and washburn studies have led to the suggestion that the colour of raw waters at treatment works may be reduced by excluding highly coloured flows from subcatchments. The design of the water collection system at Howstean and Inmoor with its series of intakes suits this form of colour management. Water colour levels in subcatchments have been related, McDonald et al., Jan 1987, so that by measuring colour at one subcatchment, the colour of the others can be approximated by means of a "look up table" and decisions taken as to which subcatchments to exclude. The effect of exclusion on the volume of water collected has also been assessed allowing reservoir managers to assess the relative merits of excluding or including waters. Clearly, if reservoirs are at capacity it is desirable to exclude highly coloured flows. This form of management is dependent on the engineering structures being present to manipulate catch waters in this way.
Manipulation of the Howstean catchment is already in progress, streams 1 and 13 (HS 2 and 14) are turned out, when there is no shortage of water, to exclude highly coloured flows. (See Water Authority Report, 2 January 1987).

In areas where these options are not available moorland management represents an alternative to the high capital costs of building such structures.

**LAND MANAGEMENT GUIDELINES**

Land management guidelines for ditching, burning and liming are directed here towards the prevention and/or reduction, at source, of colour production arising from peat; rather than the manipulation and/or treatment of discoloured raw waters.

**4.2.1 MANAGEMENT RECOMMENDATIONS IN RELATION TO BURNING.**

**FACTORS TO BE CONSIDERED.**

**WATER QUALITY**

From the consideration of water quality alone, colour and in turn, Fe and Al levels could be reduced if moorland burning practices ceased. However, this would be highly damaging to moorland ecology, recreation, revenue and possibly agriculture whilst the probability of accidental fires would increase greatly, as older stands of heather
have thick layers of litter. These fires would produce large areas of eroding peat and depending on temperatures increase colour production over large areas for relatively long periods of time; revegetation being much slower after such fires, as higher temperatures are usually reached. The resulting conditions would be significantly worse than those which 'good' moorland management practices would produce by regular burning of late building phase heather (10-15 years old), in small patches on a rotation basis.

COSTS AND LOST REVENUE
Several inter-relating costs occur between moorland management by burning and the ultimate cost of water treatment. It is apparent from this research that the burning of heather stands increases colour production, and that higher temperatures (experienced in managements burns) produce more colour than low temperature burns. If increased colour levels are created in raw water, more $\text{AlSO}_4$ is required to treat it (an added cost) and the subsequent extra amounts of sludge incur higher disposal costs. This presents two alternatives for improved management of colour, either to pay the extra capital and operational costs of treatment and disposal, or to solve the discoloration problem at source by improving moorland management by ensuring that sufficient manpower is available during the burning season to achieve a yearly quota of burning on a 10-15 year rotation (the current burning rotation at Howstean and Inmoor is a 15-20 year
Clearly, the expense of extra manpower during the burning season would be the more cost effective option.

Better moorland management should also reduce the risks and subsequent costs of accidental fires. The fire in 1976 at Glaisdale cost £46,000 to fight, control and extinguish and the consequent loss of income from grouse shooting was estimated at £5,000 per annum, whilst that from sheep grazing was put at £1,200 per annum, bringing the total to £52,200 in the first year alone. Should such a fire occur today, the total cost penalty would be in the order of £150,000 from inflation alone.

Obviously the occurrence of such fires is expensive and may also incur consequential additional water treatment costs for many years thereafter. Again obviously, the establishment of optimum management strategies is of paramount importance to Water Companies, Landowners and Tenants. Adequate control of water supply catchments is crucial in order to ensure proper management. Tenancy agreements would require comprehensive drafting in order to achieve proper management to a desired level.

ECOLOGY

The good management of moorland by burning ensures that the heather and the communities it supports, remain part of British Heathland. To abandon burning would in time largely destroy much of the heather and other plants, such
as *Pteridium aquilinum*, and *Vaccinium myrtillus*, would invade degenerated communities and become dominant. Whilst this may be preferable for water quality in terms of colour production it must be balanced in overall terms with the ecological and recreational needs and the requirements for grouse management.

By contrast, poor management or none at all, would lead to accidental fires and affect, *on a large scale*, the ecology, recreation and grouse management. Problems of erosion could also follow and in such an event it *would be preferable* to attempt to recolonise with plants, *other than heather*, which do not require management by burning, or impinge on water discoloration.

**CLIMATE**

As climate becomes hotter and drier during the summer and warmer and wetter during the winter, good heathland management becomes more important. Warmer, wetter Autumns and Springs make burning during the allowed legal season more difficult to achieve as it is traditionally carried out on cold, frosty days. These difficulties lead to postponement thus increasing the number years between rotations, which in turn, leads to hotter fires, greater risk of accidental fires and to increased colour production.
This increased colour production is additional to that which is caused 'naturally' by the increasing incidence of drought years. Furthermore the trend towards hotter summers increases the risk of accidental fires and exacerbates those processes responsible for colour production in burned patches.

RECOMMENDATIONS FOR MOORLAND MANAGEMENT, DIRECTED PRIMARILY AT WATER QUALITY, BUT ALSO CONSIDERING OTHER FACTORS.

(i) Stands should be burnt in the late building phase, when they are 30-38 cm high or 10-15 years old, (height and age depending on growing conditions). They should not be allowed to pass into mature or degenerate phases. Such strategies would reduce burn temperatures and the length of time required for revegetation.

(ii) Burning should be carried out in conditions conducive to minimising surface temperatures, that is when soil moisture conditions are high, frosty conditions being ideal. In areas where burning intervals are long it may be preferable to burn in less conducive conditions to prevent the further ageing of the stands and in turn to reduce the temperatures reached. This would require extra care being taken to ensure that fires do not get out of control.
(iii) Alternative management techniques should be considered where possible. Cutting can prove successful in building and mature phases and where access for machinery is possible. Potential compression problems can be minimised by cutting during the summer months, when poaching of the peat is less likely, as cutting is not restricted to a legal season. This option would be unattractive on grouse moors however, as the risks to nests, young chicks and the consequent impact on revenue would be high. Even on 'non grouse' moors machine cutting would threaten other nesting birds. After cutting, the clippings should be left on the moor or raked up, burnt and the ash re-spread so that nutrient supplies are not depleted. The cutting of degenerate heather would be largely unsuccessful as its ability to regenerate by vegetative growth is very low and relies on the seed bank, which is better stimulated by the passage of fire.

(iv) Grazing should be kept at recommended levels for the type of moorland being considered, especially if burning has been harsh and revegetation is likely to be slow. Research indicates that the stocking density for dry heather moor should not exceed 2 ewes per hectare, whilst on wet heath and blanket bog, the density should be less than 0.5 ewes per hectare.
Levels of other stock should also be taken into consideration.

(v) Individual burns should be small, ideally less than 2 ha, and in long narrow strips about 30 m wide as burning in strips has several potential benefits. Sheep are encouraged to disperse and feed on the numerous stands of young palatable heather which are widely distributed throughout the moor, so reducing the risk of localised overgrazing and benefiting revegetation. Burned areas also act as firebreaks and help to restrict the spread of accidental fires. The habitat for grouse is improved and revegetation of sites burnt at high temperatures would occur more quickly due to the input of seed from either side of the strip.

(vi) Where large tracts of late mature or degenerate heather occur, good management is required to maintain heather habitats and to decrease the risk of accidental fire. In such areas, and following burning or clipping, colour production could be reduced by aiding revegetation by re-seeding (or planting) with heather. Nutrient levels could also be increased by fertilization, but the use of lime to improve soil conditions should be avoided.
The above management strategies comply mostly with those proposed by the Nature Conservancy Council in their Heather Regeneration Study (1989), and allow beneficial management of both heather habitats and water colourisation. The rationale behind such strategies is deduced from the research results and the works of other authors, as discussed in Section 1.1.

4.2.2. MANAGEMENT RECOMMENDATIONS IN RELATION TO LIMING

FACTORS TO CONSIDER

COLOUR.
The proposed practise of reducing colour by liming catchments with "massive" doses, at or greater than remedial liming levels, would appear impracticable as research and the literature indicates that both colour and metal levels would increase and there would be a potential to precipitate out colour in combination with Fe and Al. This reaction is likely to be pH sensitive however as precipitates form above pH 4.5, but redissolve above pH 7 or, upon re-acidification. This would require very finely balanced management that was catchment specific; a "simple" addition of "massive" amounts of lime being uncontrolled and having a random effect if soil chemistry is not considered. In addition, the "lime effect", once in place would have to be monitored and replenished to prevent re-acidification. The necessary interval for this is
catchment dependent, but Underwood et al., (1987) have noted in their studies of lakes, that reliming was necessary every 212 days! Admittedly, the period would probably be longer for terrestrial liming.

Liming may also create alternative water quality problems, for example Kreutzer et al., (1989) and Marschner et al., (1989), have noted that liming increases mineralisation rates leading to enhanced heavy metal accumulation in soils and increased concentrations of potentially hazardous substances, Al, Fe and NO$_3$ in the soil solution, nitrate for example increasing above World Health Organisation (WHO) limits of 11.3 mg l$^{-1}$ for potable water.

**COSTS.**

Costs involved in liming include, the cost of procuring and applying the raw material and the subsequent water treatment costs, other than colour, that may result from the application of lime.

Application costs may be much higher than those in agricultural situations since many high peats are inaccessible to farm machinery and would require aerial application. Treatment costs are also likely to escalate for, even if colour is reduced, the process is reversible, resulting in high colour flows when re-acidification occurs. Therefore to maintain the 'lime effect' repeated applications would be required. If liming increases colour
then obviously treatment costs will increase, negating the purpose of liming in colour terms, although it would reduce levels of inorganic Al and Fe, but not levels of organic Al and Fe. Additional costs and other problems could also arise as liming is likely to increase bacterial numbers in raw waters.

ECOLOGY
The application of massive doses of lime to upland peats will severely affect the ecology of moorlands, in direct conflict with conservation. However, the consequent reduction in levels of inorganic aluminium in waters is beneficial to fish as organic forms of aluminium do not affect them.

RECOMMENDATIONS.
Large scale liming is not recommended as a management technique for colour reduction for the research shows that liming increases colour. This directly conflicts with the proposed practise of terrestrial liming to mitigate acidification. Liming, whilst increasing pH and reducing levels of toxic aluminium, Jenkins et al., (1991), can lead to drastic ground and surface water contamination, resulting in the nitrification, mobilisation and translocation of heavy metals from the humus layer and the accumulation or mobilisation of colour and associated Al and Fe. Therefore, liming should not be practised before the potential for undesirable side effects has been
carefully considered. In addition, the effects of re-acidification also need to be considered, Marschner et al., (1989) suggesting that, owing to the high rate of lime dissolution at some sites, it could occur within 10 - 15 years and result in greater water quality problems than existed prior to liming, unless lime is re-applied. This conflict clearly indicates the need for catchment liming projects to include consideration of a much wider set of consequences upon water quality, than only the increases in pH and Al levels.

4.2.3. MANAGEMENT RECOMMENDATIONS IN RELATION TO DITCHING.
In terms of colour management, ditching should be discouraged as any form of ditching decreases soil moisture (as it is designed to do!) thereby leading to the processes which increase colour production.

In terms of improving heather growth for grouse it is questionable whether ditching is beneficial, as it is of limited benefit to heather regeneration, Coulson et al. (1990). In addition, it reduces the invertebrate food supply of red grouse and other moorland birds and the production of Eriophorum seed heads, an important food supply for young chicks (personal communication F. Booth and D. Newborn, North of England Grouse Research Project, The Game Conservancy).
Significantly, the Heather Regeneration Study of The Nature Conservancy Council (1988), strongly recommends that blanket bog and heather moorland should not be drained or moor-gripped, since not only does it have limited benefits for heather, it also damages the ecology of moorland habitats.

Drainage also increases sediment yields, which leads to further water quality problems such as increased sediment loads; damaged salmonoid spawning grounds; lower reservoir storage capacities and consequently causes additional water treatment problems. Erosion leading to increased sediment yields is not restricted to artificial ditch systems, the intensification of natural drainage networks also occurs, resulting in the dissection of head waters, streams and watersheds, leading to the development of peat haggs. This in turn initiates the processes involved in the oxidation of peat and thereby increases colour flows.

Where drainage is necessary, for forestry or pasture improvement, steps should be taken to limit the effects and sensitive catchments should be avoided. Buckley et al, (1987), reported on studies at Anglers’ Retreat, Wales, where 'hard' ploughing was compared to that of 'soft' ploughing in terms of colour generation. 'Soft' ploughing was found to have a lesser effect on colour production, most probably due to the smaller effect on the water table produced by contour ploughing as compared with the steep
gradient drains produced by 'hard' ploughing. The fact that flows from 'soft' ploughing also pass through soils adjacent to streams, may also have the effect of reducing colour by precipitating, filtering, or by absorbing colour onto soil exchange sites. Although this is speculative it does seem plausible as colour flows are sometimes seen to decrease when leached through peat, as indicated by the large scale leaching experiments described in Sections 3.1.1. and 3.2.1. The possibility of mole drains which limit drainage to the surface layers should also be explored as drain linings restrict the down cutting of drains through erosion and sediment transport, and thus aeration is restricted to the surface layers.

4.3. CONCLUSIONS DRAWN

4.3.0. INITIAL SITUATION

Although spatial and annual trends have always been evident in the discoloration levels of raw water, the highest ever level was recorded in 1985.

Examination of these trends indicates that discoloration in raw water from upland peat catchments, though by no means a new phenomenon has shown higher and more varied levels since 1976.
Whilst there is an apparent correlation between the severe droughts of 1976 and 1984 and the highest colour flows in 1976/77 and 1984/85, overall levels have not fallen to pre 1976 levels.

Records at treatment works prove that not all catchments produce colour in similar amounts or with similar pattern changes. This suggests that fluctuations in colour level are potentially caused not only by the occurrence of drought conditions, but also that other factors are at work, including differing physical characteristics.

It is however, the potentially differing anthropogenic causal effects which form the basis of this research.

4.3.1. RESEARCH CONCLUSIONS

PHYSICAL FACTORS
The main physical factor was found to be soil type. Catchments containing a high proportion of deep peat exhibited high colour flows compared with those having thin organic soils. Within this relationship however, other fluctuations occurred and were not explained merely by the presence of deep peat.

As all other factors were constant, moorland management strategies were examined to assess their possible impact on colour generation. These strategies were (1) burning (for
grouse management) and (2) moorland gripping which was examined on a large scale and its density was found to be positively correlated with increasing colour flows. These examinations initiated further detailed studies to investigate the colour flows which they caused.

Liming was also examined, it had been suggested that this practice would reduce the acidity and therefore inhibit the production of colour, it had also been suggested by the Yorkshire Water Authority that the acidification of catchments by acid rain had increased colour flows.

4.3.2. EFFECTS OF BURNING, DITCHING AND LIMING ON THE PRODUCTION OF SOLUBLE COLOUR IN SUPPLY.

HEATHER MANAGEMENT BY BURNING was found to increase colour production over that of non-burned moorland.

The magnitude and timescale of colour production were related to fire characteristics of which temperature was the most significant. The distinction is drawn between hotter (approx 600°C) burns which produce more colour than cooler burns (approx 300°C), although it does not follow that severe fires follow this pattern.

DITCHING, DONE TO INCREASE DRAINAGE, by drawing down the water table also promotes aerobic soil conditions which causes increased production of colour.
ARTIFICIAL APPLICATION OF LIME (LIMING) DOES NOT REDUCE COLOUR PRODUCTION because it raises the pH thereby improving soil conditions and in turn increases microbial activity. The products of decomposition FA and HA in turn being more soluble at elevated pH.

4.3.3. POTENTIAL PROCESSES

PROCESSES WHICH POTENTIALLY INCREASE COLOUR are primarily linked to fluctuations in soil moisture. As burning and gripping reduce moisture content and increase aeration, increased microbial activity follows. This gives rise to increased decomposition and the production of humic and fulvic acids, which are then released by seasonally increased moisture, giving rise to coloured flows. Although on a much smaller scale, these mechanisms are the same as those created by drought conditions. (These larger scale processes being researched by Mitchell, (1990).)

LIMING ALSO INCREASES COLOUR PRODUCTION by microbial activity, initiated by increased pH rather than a decreased level of soil moisture, and chemical effects on humic and fulvic acid are also involved.
PROPOSED MANAGEMENT STRATEGIES TO REDUCE COLOUR IN RAW WATER

Large scale natural effects of colour production can only be managed by excluding highly coloured flow from raw water supply. Small scale anthropogenic effects can be managed by improved moorland management, to achieve improved water quality.

RECOMMENDED STRATEGIES THEREFORE ARE:

(i) The drainage of deep peat by gripping should be discontinued or at least controlled at minimal levels. 'Soft' ploughing should be adopted instead of 'hard' ploughing where some type of artificial drainage is unavoidable.

(ii) Heather management by burning should be carried out in the 'late building phase', i.e. at 10 to 15 years old. This controls the burn temperature and minimises colour production. Colour management by avoiding burning is not an option due to the increased risk of accidental fires.

(iii) To avoid the use of lime as a means of managing the production of colour.
These strategies are strongly recommended in order to improve raw water quality by reducing colour production. Their adoption should minimise the colour produced by the scale of processes which this research addresses.

It is clear that increases in colour production caused by larger scale natural effects will need to be recognised as an important factor in policy making for water treatment. However, this does not detract from the advisability of adopting these 'small scale' recommendations forthwith. Whilst these recommended management strategies are directed towards controlling water colour it is realised that their absolute adoption would conflict with other moorland management strategies directed towards achieving other objectives.

4.4. **FURTHER WORK.**

**BURNING.**

Further work is desirable to examine the processes of colour production arising from burning, addressing the topics covered in Fig. 4.19 and specifically in the following areas:

1. Soil moisture, both permanent and provisional, relating to;
   The effect of ash on infiltration capacity. Water repellency and its related effect with temperature in terms of waxes and resins. The biological effect, leading to the
formation of crusts and water repellent layers. The relative tensions at which soil water is held; and, rewetting abilities.

(ii) Decomposition; As it is affected by temperature and soil moisture on the stability of humic substances. Measurement of microbial populations and activities, e.g., by C:N ratios, respiration or plate counting techniques.

(iii) Microclimate, requiring detailed, extensive study of; The time factors involved in initiating increased colour production. The permanence or otherwise of such increases; and, The links between these processes and revegetation.

(iv) Burning, considering the differing effects of; Managed burns; Severe burns (usually accidental); Field sampling and results; and, Laboratory simulation of 'natural' burns, by flaming. To cover an appraisal of the processes involved in each case.

**LIMING.**

Additional work suggested is again mostly process based and relates to the processes listed in Fig. 4.20.

(i) To repeat the liming of cores taken from the field, simulating 'field' dosages of 0, 2, 6 and 10 tonnes per hectare.
(ii).
Examination of the effect of increased pH on microbial numbers and activity; Identifying the scale and extent of subsequent decomposition; and, Identifying the time scales involved.

(iii).
Chemistry of humic substances. To assess the effect of pH alone on the solubility of HA and FA; To discover the implications for metal solubility; and, To identify the specific responses of specific peat deposits.

(iv).
Metal organo-complexes. To discover their role at different levels of pH; Examining the precipitation/solubility of humic substances; and, Determining whether colour is 'true' or 'apparent'.

DITCHING.
Within the consideration of the processes listed in Fig. 4.21., to address the following aspects.

(i).
Soil moisture. Evaluating its relationship with the extent of water table draw-down; Relating levels of colour to the magnitude and duration of wetting/drying cycles; and, Examining the effects on the conditions which cause and encourage decomposition.
(ii). Erosion. To determine changing rates of erosion; Identify the exposure of fresh surfaces; and, To assess consequent colour generation.

(iii). Afforestation. Examination of the effects on soil moisture of forestry, increasing decomposition; and clear felling on elevating depressed water tables, leading to the flushing of stored colour.

Following this research, the National Rivers Authority have funded a research project to address the effects of afforestation.

4.5. RESEARCH CRITIQUE.

With the hindsight which inevitably arises after a long research programme the following desirable changes and requirements can be identified.

Improved management of time would allow repetition of experiments and possibly better validation and evaluation of results.

Detailed and thorough consideration of all three forms of Management with all the attendant topics and aspects of enquiry, has resulted in the available research time for each subject being diminished. Consequently, small scale process studies were not undertaken, most attention was
paid to the management of colour, to satisfy the aims of the research.

Attention to Management took priority over Process which was not entirely desirable even though the objectives of Process were being covered by Mitchell (1990).

The literature researched, considered and covered in Chapter 1 was extensive but the heavy workload it represented is justified, as it is highly relevant to the topics of Burning, Ditching and Liming. The effects of these practices needed to be fully understood, to enable colour management strategies to be formulated.
APPENDIX A

(1) Sketch Map of the Soils in the Washburn Valley - taken from the S.S.E.W. 1:250 000 North Sheet.

(2) Photograph of Leaching Apparatus.

(3) Analysis of Rainfall, Upper Nidderdale for Sulphate, Phosphate, Nitrate and Chloride.

(4) Neutron Probe Calibration for Inmoor Peat.


(6) Blocks After Treatment, Foreground the Limed Block, Middle the Burned Block and the Droughted Block.
Approximate pedology for the Washburn Valley.

Taken from the S.S.E.W. 1:250 000 Northern Sheet.
ANALYSIS OF RAINFALL: UPPER NIDD

SULPHATE.

SO₄²⁻: 0.90 - 0.78 pH

SO₄²⁻ (ppm) vs pH

pH

2.50

3.00

3.50

4.00

4.50

5.00

15.0

10.0

5.0

0.0
ANALYSIS OF RAINFALL: UPPER NIDD PHOSPHATE.
ANALYSIS OF RAINFALL: UPPER NIDD NITRATE.
ANALYSIS OF RAINFALL: UPPER NIDD. CHLORIDE.
NEUTRON PROBE CALIBRATION FOR INMOOR PEAT

\[ \text{MVF} = 0.1818 + (0.4949 \times \text{R/RW}) \]
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