FIELD OBSERVATIONS OF LIMESTONE WEATHERING AND EROSION IN THE MALHAM DISTRICT, NORTH YORKSHIRE

S. T. TRUDGILL

Department of Geography, University of Sheffield S10 2TN

Abstract

Measurements of present-day weathering and erosion processes are described in the Malham limestone district of North Yorkshire. Attention is focussed on processes operating in the soil profile as much of the solutional erosion in a limestone landscape takes place in this zone. Since solutional weathering potential is provided by acids, measurements focus on soil acidity, testing the hypothesis that erosion will increase with soil acidity. This was found to be generally true, but was qualified by the effects of soil depth and soil water flow. The implications of the findings for solute levels in runoff and longer-term landscape evolution are discussed.

INTRODUCTION

THE limestone landscape around Malham Tarn Field Centre (Fig. 1) is striking for its bare rock pavements, its cliffed scars and steep screes. Malham Cove forms the centrepiece of the scenery, backed by wild stretches of open country where thin patches of shallow limestone soils alternate with deeper pasture soils and bare rock. The rivers and streams run from the bleak, peat covered hills, sinking as they reach the limestone, reappearing later in karst springs, as already described in Smith and Atkinson's (1977) paper. Malham Tarn itself lies perched on an outcrop of impermeable rock, forming a wide stretch of open water—unusual in limestone areas. This diverse landscape gives rise to a number of habitats for animals and plants as well as providing a setting for the activities of man. The landforms and soils form the basic physical framework of the area and these can be studied both in terms of their origins in the past and also how they are developing at the present day.

Landforms and soils evolve over many thousands of years and often we can only understand their origins by piecing together fragments of evidence. The papers written by Moisley (1955) and Clayton (1981) on the Malham limestone area have reviewed such pieces of evidence. The authors have concluded that the area shows the effects of glacial action, leaving behind evidence, for example, in the form of scoured glacial rock pavements and glacial deposits in moraines. The effects of post-glacial solutional action can also be seen, with small runnels forming where rain water or acid soil water flows over limestone. But as well as asking the question "how did the present landscape evolve?" an equal one is "what is happening to it now?". The interest in this question is that by attempting to answer it we actually measure and observe the processes which are currently helping to shape the landscape. In making measurements and observations at the present-day, we cannot necessarily suggest anything about the origins of a landscape, and it is important to have *both* questions in mind when walking around and studying the landscape: "How did it get there?" and "What is happening to it now?". In this paper, we shall look at the present patterns of soils and landforms. The reader can also refer to



the two papers mentioned above and to another on soils by Bullock (1971). Then, several techniques of study will be described in outline, whilst details of the methods are given in the Appendices. Trudgill (1983) and Briggs (1977*a*, *b*) will be useful for further reading. The application of these techniques to a variety of geomorphological and soils problems will be discussed followed by interpretation and discussion of the data. One particular focus is the role of a soil cover in weathering. The importance of weathering under soil is confirmed by the data in Table 1: at least 50% of overall erosion rates in limestone areas is concentrated in the top few metres of soil and shallow bedrock. This emphasises the importance of the study of erosion under soil and of variations of erosion with soil type, as discussed further by Trudgill (1985, Chapters 3 and 4).

Агеа	Overall Rate	Remarks
Fergus R, Ireland	$55 \mathrm{m^3} \mathrm{km^{-2}} \mathrm{a^{-1}}$	60°_{\circ} at surface Up to 80°_{\circ} in top 8 m.
Derbyshire	$83 \text{ m}^3 \text{ km}^{-2} \text{ a}^{-1}$	Mostly at surface
North-West Yorkshire	$83 \text{ m}^3 \text{ km}^{-2} \text{ a}^{-1}$	50° at surface
Jura Mountains	98 m ³ km ⁻² a ⁻¹	58°_{\circ} at surface 37°_{\circ} in percolation zone
Cooleman Plains New South Wales, Australia	$24 \text{ m}^3 \text{ km}^{-2} \text{ a}^{-1}$	75°_{\circ} from surface and percolation zone

Table 1. Rates of erosion for 5 temperate soil covered catchments (after Atkinson & Smith, 1976)

 $m^3 km^{-2} a^{-1} = cubic metres per square kilometre per annum.$

Soils, Weathering and Erosion

Soils, weathering and erosion are closely linked since, in the first place, soils develop as a result of the weathering of parent material (in this area, mostly bedrock and glaciallydeposited drift), under the influence of climate and vegetation. In the second place, the nature of the soils which evolve, in turn, influence the nature and extent of the weathering of their parent material and the bedrock. Climate acts as an important independent variable, influencing not only vegetation but also the amount of water which drains through the soil. Such drainage acts as an important influence upon solutional erosion since it is this drainage water which carries away the dissolved products of weathering reactions. The main linkages between soils, climate, vegetation, weathering, erosion and parent material are illustrated in diagrammatic form in Fig. 2. Soils can thus be interpreted in terms of the interaction between parent material below and climate and vegetation above. At Malham, acid soils have developed under conditions of high rainfall and where there is little limestone in the parent material (e.g. glacial drift derived from acid millstone grit). Alkaline soils, rich in calcium carbonate, have developed where there is abundant limestone present in the parent material. This contrast in soils, together with areas which are free of soil, provides a contrast in weathering environments. Weathering systems can be thought of in terms of the potential which the environment provides for weathering (Fig. 3). The greatest amount of weathering takes place under acid conditions and therefore water draining through acid soils has a high weathering potential. One of the tasks in a study of present day weathering is, therefore, to attempt to understand the variations in weathering potential which exist in different environments, such as those shown in Fig. 4. Measurements of soil and water acidity are going to be an important step in any such evaluation. Subsequently, assessments of potential weathering can be compared with actual rates of weathering, types of erosion and also the amounts of dissolved weathering products being lost in solution—as suggested diagrammatically in Fig. 3.

In this paper, soil, stream and rainfall acidity are compared in terms of their relative erosion potential. Then, since acidity is carried to weathering sites by running water and weathering products are also carried away from the sites by water—the entry of water into soils (infiltration) is also assessed, together with comparisons of water flow rates in different soil types. Erosion potential data and water flow data are then compared with



measurements of actual erosion rates under different soil types and in areas where there is no soil. Finally, solute concentrations in runoff waters are examined and their relationships with erosion rates and potential are discussed. Thus, the paper follows the three



Environments of weathering in a limestone area.

points of study shown in Fig. 3—with the evaluation of weathering potential, surface lowering and losses in solution. First, however, it will be useful to provide a summary of the main features of the geology, landforms and soils of the study area and of other features relevant to the topics of this paper.

The Malham Tarn Area

The Malham Moor limestone area is in northwest Yorkshire on a part of the Pennines known as the Craven uplands (Fig. 1). Much of the area is a high-level limestone plateau which contains some of the classic karst of the British Isles (Clayton, 1981; Moisley, 1955; Taverner, 1981). The Moor extends from Darnbrook Fell (624 m) in the north to Malham Tarn in the south. The Ribble–Aire and Ribble–Wharfe divides form the western boundary and Parson's Pulpit (538 m) the eastern edge. The southern part of the Moor forms the catchment for the Malham Tarn basin but much of the area is drained by one stream, Cowside Beck and its tributaries, flowing northeastwards into Littondale. The Moor rises to 668 m on Fountains Fell in the northwest and falls to 305 m where Cowside Valley leaves the Moor.

The surface geology is shown in Fig. 5. The geological succession involves a near horizontal sequence of Carboniferous rocks. Structurally, Malham Moor is part of the Askrigg Block, a rigid fault bounded block of basement rocks related to an underlying granite intrusion. The geological sequence is described by Shaw (1983), Rayner and Hemingway (1974), Waltham (1974) and Taverner (1981). The basement rocks are a series of Ordovician and Silurian sandstones and silts, part of the Horton formation, folded into tight east-west folds with the finer sediments cleaved to form slates. They are exposed as small inliers to the north of the North Craven Fault, and impervious



The Geology of the study area (adapted from Shaw, 1983).

slates support the waters of Malham Tarn on the southern edge of the Moor. The Carboniferous sequence rests unconformably on the basement beds (Fig. 6).

The western (lowest) member of the Carboniferous sequence is the Great Scar Limestone. This consists of 100–205 m of pure crystalline limestones which are relatively consistent laterally but show considerable vertical variation (Sweeting, 1974). The limestones are pale grey to cream in colour and their composition is illustrated in Table 2. They are generally fine grained bioclastic sediments, 50% of the volume consists of Foraminifera, fragments of shells and crinoid ossicles (Waltham, 1974). The ossicles often stand proud after dissolution of the matrix. The matrix can be a fine calcite mud in the micrite limestones and biomicrites or coarse sparry calcite in a sparite or biosparite limestone. Micrite refers to fine grained calcareous silt-sized particles and sparite to the



Geological section from north to south in the study area (adapted from Shaw, 1983).

Table 2. Chemical analyses of Great Scan Limestone (after Waltham, 1974)					
	A	В			

CaCO ₃	99.05	93.67
MgCO ₃	0.46	4.38
Fe ₂ O ₃	0.06	
Al_2O_3	0.06	
CaSO ₄	0.05	
SiO ₂	0.15	
Insoluble	_	1.95

A-limestone from Horton-in-Ribbledale

B-means of 10 limestones from various localities.

presence of crystals of calcite spar, often around 1 mm long and closely interlocking. The micrite limestones are porcellanous, that it is they appear like china upon fracture. The beds may be up to 15 m in thickness. The more resistant sparry limestones have thicker beds, with few joint planes. This renders them less open to water entry and thus less prone to dissolution and frost action than the more thinly bedded and heavily jointed micrite (Fig. 7). Joint planes in the micrite are normally 0.25–0.5 m apart, while those in the sparite are 0.5 m–1 m apart (Sweeting, 1972). Sweeting indicates that the texture of the limestone also influences the rock porosity and therefore the entry of water into the rock itself, in addition to water entry down joints. Micrites have a porosity of 2°_{0} or less: sparites, 5–8% and the most open textured are the biosparites and biomicrites with a porosity of between 15 and 25°_{0} .

Limestone outcrops to the north and east of the Tarn and becomes increasingly obscured with superficial drift deposits in the north and west. In addition, above the Great Scar Limestones are the sediments of the Yoredale series, repeated units of limestone, shale, sandstone and coal resulting from rhythmic or cyclic sedimentation. The Yoredales are overlain by Millstone Grit, a sequence of shales, sandstones and thin coals, with the most resistant member being a coarse feldspar-rich sandstone. These rocks form the summit plateau of Fountains Fell and Darnbrook Fell, and are the source area for much of the acid run-off water entering the limestone outcrop below. The whole Carboniferous succession has a slight northerly dip and this, together with the rise in altitude means that the entire vertical sequence is encountered on a southeast-northwest transect of the Moor (Fig. 6). Prior to glaciation, the Askrigg Block and its overlying



Section of rock face, showing well jointed micrite limestone between layers of more massive sparite limestone.

succession was uplifted relative to the Craven and Lonsdale lowlands and the rocks were deeply weathered, providing local material which glaciers could erode and deposit as till (King, 1976, and Clayton, 1981).

Glaciation

The Devensian (last) glaciation had the most obvious effect on the landscape. This was the period of the Main Dales Ice advance, although the whole area had been ice-covered, and considerably eroded, during at least one earlier glaciation. There was enough high ground on the Askrigg Block for a local ice cap to form and to prevent other ice masses, such as the Scottish Ice from entering the area (King, 1976). Glaciation removed the weathered mantle giving rise to a pattern of small scars and benches. Ice moved from northwest to southeast although some may have been deflected northeastwards along the lower part of Cowside Valley. As a result, much of Malham Moor is covered with glacial drift, which is several metres deep in places. The resistant sandstones and limestones form the major constituents of the drift while the matrix is mainly from the weaker bands of rock in the local sequence (King, 1976). Both acid (gritstone/sandstone) and alkaline (limestone) drifts occur in the area, mixed in varying proportions.

To the south and east the more distinctive landforms of glaciated karst are to be found: bare pavements, scars and dry valleys. The remainder of the Moor, with its thick cover of superficial deposits, is still very much a landscape of surface drainage.

Present landscape processes

In terms of present landscape processes, dissolution is very active in the soil and superficial deposits at the soil-limestone interface through the action of percolation waters. It is also active where acid, peat-derived streams leave the Millstone Grit fell top areas as surface streams and encounter the limestone. The streams are the major routes for the transport of solutes. Sediment transport is evident on the drift slopes from the occurrence of small slips, slumps and terracettes. Surface runoff and soil wash are highly localised but on the steeper slopes mass movement is extremely active and material reaches the stream from both landslides and soil creep. Slope and channel forms are still in the process of adjusting to present conditions and show a strong legacy from the past. There is evidence of one or more phases of downcutting associated with base level changes or increased discharge during periglacial conditions. Most streams are misfits in a glacial and periglacial landscape.

Climate

The present climate is typical of the Pennine uplands with cool, wet conditions (Manley, 1979). Data are available from the Malham Tarn Meteorological Station, next to Tarn House (395 m), and more limited records from Fountains Fell (660 m). Due to the ameliorating effect of the Tarn, the south facing site, and the shelter provided by the surrounding woodland, the Tarn figures are probably more typical of the lowest part of the Moor and Cowside valley than of the higher moors. At Malham Tarn, monthly mean temperatures are all above freezing with a range of 12°C, whilst the higher Fountains Fell station shows a range of -1.0° C to 10.5° C with two monthly means below freezing (Manley, 1979). The mean annual precipitation (1941–1970) is 1483 mm at Malham Tarn, rising to approximately 2000 mm on Fountains Fell. Potential evaporation is of the order of 500 mm at Malham Tarn (Bullock, 1971). The excess of precipitation over evaporation means that leaching of soils is encouraged. In addition, rainfall can contain sulphur derived from industrial sources to south and south west, and, as 34% of the winds recorded in the area come from that direction, acidification of rain can be expected. The rainfall for 1957–1960 had a mean pH of 4.6 with a range of 3.8–6.2 (Raistrick and Gilbert, 1963). Rainfall equilibriated with atmospheric carbon dioxide alone can be expected to have a pH around 5.6. Thus, the mean value of 4.6 shows evidence of acidification and the range given above demonstrates both an increase and a decrease in acidity, the latter very probably in relation to locally derived windborne limestone dust.

Soils and vegetation

On the Great Scar limestone the most widespread soil is a mesotrophic (moderately nutrient rich) brown earth (Bullock, 1971), developed on thin glacial drift deposits. Rendzinas (thin organic limestone soils) occur on pavement edges and on the steep valley sides where the drift cover is thin or absent. A rendzina is both organic and calcareous and accumulates through the formation of stable calcium-humates which are resistant to further breakdown under alkaline conditions. Under wetter and colder conditions limestone rankers occur; these are raw, acid humus soils where the organic matter does not decay because acidity and low temperatures inhibit biological activity; acidity is maintained by the high rainfall. On the thicker drift-covered slopes, *peaty gleyed podsols*, *peaty* gleys, podsolised brown earths, and acid and calcareous brown earths dominate*. The podsols show evidence of iron movement underneath wet, peaty organic layers and the gleys show evidence of sporadic oxidation of reddish iron mottles (iron III [or ferric iron]) in an otherwise anaerobic, waterlogged soil where grey coloured reduced iron (iron II [or ferrous iron]) is present. The brown earths vary in their stone content and acidity, the latter depending on the mineralogy of the stones (acid if gritstone or alkaline if limestone). They are found on the steeper slopes, especially with acid-brown earths on *Names of soil types. See the note on p 234

slopes of sandstone rich drift. Peaty gleys tend to occur on clay rich drift. Peat occurs on the Millstone Grit uplands. The whole area is mainly rough grazing for both sheep and cattle but some pasture improvement with liming and fertiliser application has taken place in recent years. A common pattern is for thin limestone soils and thicker limestone drift soils to stand out as greener swards, formed of the grasses *Festuca ovina* (sheep's fescue), *Agrostis capillaris* (= A. tenuis) (common bent), and *Sesleria albicans* (= S. *caerulea*) (blue moor grass) mixed in varying proportions. The acid soils on the sandstone or leached limestone drifts appear rougher and paler with *Nardus stricta* (mat grass), *Deschampsia flexuosa* (wavy hair grass) and *Juncus squarrosus* (heath rush). On the peaty soils, *Calluna vulgaris* (heather), *Vaccinium myrtillus* (billberry) and *Eriophorum vaginatum* (bog cotton) occur. Thus a variety of acid and alkaline soils may cover the limestone, presenting contrasts in the weathering environment both for the stones within the soil and the bedrock beneath it.

Field sites

The two main sites were a calcareous slope at Cowside Beck and a more acid slope at Darnbrook Beck—both of which are shown on Fig. 1. Several others have also been studied and will be mentioned later in the text.

A typical slope profile at *Cowside*, the calcareous slope, is one where the crest is gently convex, often showing a marked steepening just above the long rectalinear or slightly convex mid and main slope element. The maximum angle is 35° . The slope base shows a trace of concavity before merging into the flood plain. The slope material appears to be largely of soliflucted drift, or "head". It is composed of finely-divided angular limestone fragments, mostly less than 6–8 cm in diameter, with occasional stones up to 20 cm in diameter. The pale brown-whitish-grey matrix consists of very fine limestone flakes, 1–2 mm or less in diameter, and grains of calcium carbonate. When the water table is high, the matrix forms a sludge but under dry summer conditions it becomes firmly cemented. On parts of the slope there are large pieces of angular head fragments present, solidly cemented with calcium carbonate. The stone content of the deposits is dominantly Great Scar limestone with occasional sandstone fragments.

The soils are rendzinas and brown earths of sandy clay-loam texture, with the rendzinas on the steeper mid and base slope sections with brown earths on the slope top. The former have thin, dark grey-black humose A horizons, 10-20 cm in depth with a moderately well-developed granular or crumb structure. Below this, a yellowish-brown to brown incipient B or B/C horizon is sometimes present. The brown earths show well developed A and B horizons, moderately structured and often containing one or two sandstone erratics. All the soils are stony but within the parent materials there is often a gradual increase in percentage stone content 50-60 cm below the surface, accompanied by an increase in compaction. Typical soil profiles are shown in Appendix 1.

At the Darnbrook site, the acid slope, drift (derived largely from the Millstone Grit) mantles the limestone. The Darnbrook valley is deeper than the Cowside valley and the slopes are consequently longer than those of Cowside by 10-20 m. Valleys slopes are steeper, up to 45° . There is evidence for there having been more intensive water erosion in the past with a series of gullies dividing the hillside into ridges and hollows, some large enough to carry distinct streams during heavy rain, others acting as seepage lines with water occasionally coming to the surface for short distances. The surface expression of the gullies decreases downslope as the hillside steepens below the crest and, at the base of the largest ones, debris obscures part of the flood plain in the form of an alluvial fan. The

slopes between the gullies in which field work has been carried out are steep, straight or slightly convex and field observations suggest that the parent materials of the lower parts include reworked slope material transported as gully wash. The slope crests tend to be less convex than those of Cowside, steepening more quickly into the long rectalinear or slightly convex main slope. Again there is the beginning of a concavity at the slope base.

The slope parent materials are more variable than those of Cowside and appear to be a complex mixture of drift and rubbly head. On the midslope, there are patches of a limestone-dominant head similar to Cowside but over most of the slope there are high sandstone contents and clay rich soils. The soil type is brown earth of sandy clay loam texture, often over deep drift. Apart from small areas where the soils show signs of podsolisation under *Nardus stricta* grass and *Vaccinium* the soils have a thicker, less humose A horizon than those of Cowside. Most soils have a mull humus, typically dark greyish brown-dark brown in colour and up to 25 cm deep. Some of the brown earths show increasing clay contents down the profile and tend to be more poorly structured and less stony than at Cowside. Again, the percentage stone content increases down the profile. Transitional soils between earths and rendzinas occasionally occur on the steeper slopes and again show the stony B/C horizon but with a more pronounced matrix of insoluble mineral particles rather than being mainly calcium carbonate. Typical soil profiles are shown in Appendix 1.

SOLUTIONAL PROCESSES AND WEATHERING POTENTIAL

Limestone is dissolved by acid water, but the types of water—rain, stream and soil water—all vary considerably in their acidity, and the sources of acidity may also vary considerably. It will, therefore, be important to consider, firstly, the general principles of limestone dissolution and then, secondly, to see how the principles apply in different situations.

There are two main sources of acidity in natural water: firstly, the solution of gaseous carbon dioxide in water and secondly, organic acids produced during the decay of leaf litter. Taking the first of these, the description of the dissolution of limestone is one where carbon dioxide dissolves in, and reacts with, water to produce hydrogen ions (H^+) and hydrogen carbonate ions (HCO_3^-) . The hydrogen ions combine with carbonate ions $(CO_3^{2^-})$ derived from the dissociation of calcite $(CaCO_3)$ in the limestone, giving further hydrogen carbonate ions—and calcium ions (Ca^{2^+}) —in solution.



Since two HCO_3^- ions are produced by the reaction, the HCO_3^- ion has been referred to as the bicarbonate ion, but it is more accurately described as the hydrocarbon carbonate ion.

It can be seen from the above reaction that a crucial step is the combination of H^+ , derived from $CO_2 + H_2O$, with CO_3^{2-} derived from the limestone. It is an important point that the H^+ ions can also be derived from other sources as well as carbon dioxide,

notably from the dissociation of organic acids which are produced during the decomposition of humus in the soil. For this reason, it can be argued that measurements of the hydrogen ion concentration in soils can be as useful as an indicator of the potential for limestone weathering as measurements of soil carbon dioxide. Measurements of hydrogen ion concentration are termed pH measurements (see Appendix 2). It is easier to measure pH than soil carbon dioxide. Therefore, in this paper, an attempt will be made to assess the usefulness of pH measurements as an indicator of weathering potential. If such a relationship can be established, this will be useful in later assessments of the spatial distribution of erosion rates in relation to soil types since soils are readily mapped in terms of acidity, rather than in terms of CO_2 (and, indeed the relationships between soil type and soil CO_2 levels are not widely known). There is already support for the use of soil pH to evaluate weathering potential from the work of Trudgill (1977a) in Jamaica where the erosional weight-loss of limestone tablets placed at the soil-bedrock interface (a method described further below) was poorly correlated with measurements of soil CO₂ concentration but well correlated with soil pH measurements. This was partly due to the fact that the highest erosional losses were under open, porous leaf litter soils where (a) organic matter provided most of the acidity potential for weathering in the form of organic acids and (b) carbon dioxide could readily diffuse out to the atmosphere, giving low CO₂ concentrations, despite high CO₂ production from leaf litter decay. Indeed, soil porosity is a vital consideration as it is important to note that often the highest levels of carbon dioxide are found in soils of low permeability because the gas cannot escape. However, this low permeability also means that water percolation is hindered. This, therefore decreases erosion because acidity potential cannot be carried down easily through the soil to the limestone, nor can any weathering products be moved easily in solution. This means that any weathering products accumulate in the soil, leading to a lowering of erosion rate, despite high CO₂ levels. Thus, assessments of pH, soil permeability and water flow rate can be as important, if not more important, than measurements of CO₂ levels (Trudgill, 1985, Ch. 3). Carbon dioxide levels have been measured by the use of a Gastec probe (Trudgill, 1983, p. 91). Clearly, the general hypothesis under test is that erosion will be greatest under acid soils.

The supplies of acids in a soil can be assessed by two further measurements: *buffer* capacity and aggressiveness (Appendix 3). Buffer capacity is a measure of the resistance of a soil to changes in pH when an acid or an alkali is added. The supply of acids in a soil is measured by adding alkali progressively to a soil-water mixture; where there are low supplies of acids, the soil rapidly becomes alkaline but where there are high supplies of acids, the soil continues to give an acid pH reading, despite the addition of alkali. The more the soil continues to give an acid reading when alkali is added, the greater the reserves of acidity within it. Aggressiveness is a further measure of the acid reserves in the soil: powdered limestone or pure calcium carbonate is added to a soil-water mixture. The potential for limestone dissolution, or "aggressiveness", is indicated by the amount of pH change at the end of this addition, (i.e. when no further pH change occurs despite continued addition). Soils with a high aggressiveness show a large pH change from acid to alkaline when the hydrogen ions in the soil have been used-up in reacting with the added powder. With little aggressiveness, little pH change is seen. In this study, weathering potential has been assessed using measurements of pH, aggressiveness and buffer capacity. In addition, assessments have been made of water flow and soil permeability (by the measurement of infiltration rates) and weight-loss of gypsum tablets, as described in Appendices 4 and 5.

Soil pH and calcium carbonate

The data for acid soils at Darnbrook and alkaline soils at Cowside are shown in Figs 8 and 9. As well as illustrating the major differences between the two sites (Fig. 8), it is evident that the patterns are not necessarily simple. While there is a general trend to greater acidity upwards in the soil profile (Fig. 9), there are also some more acid readings below less acid readings at one of the Darnbrook sites (3, a podsolic soil); moreover, there is not a simple or uniform change in pH downslope. However, there is evidence that the Cowside slopes measured are acid only in the upper profile towards the slope crest in 3 of the 4 transects. For Darnbrook 3, the podsolic soil is acid throughout, at site 2 the surface soil is acid for the entire slope but only for the upper slope at site 1.

These data mean that any pH-related assessments of weathering potential and erosion rate will not be simple. It can be predicted that there will be variations downslope and downprofile and that the variations will not always be regular. In fact, spatial variation is often a characteristic of most soil properties and pH is no exception. This must always be borne in mind when soil studies are being made.

Soil pH data were found to be related to soil CO₂ data. Under the most acid soil with peaty surface horizons the data range (30 observations) was $0.5-1.5^{\circ}_{0.0}$, but with most values between $1.1-1.5^{\circ}_{0.0}$. For the less acid, calcareous soils the range was $0.2-2.0^{\circ}_{0.0}$ but most samples were in the range $0.4-0.9^{\circ}_{0.0}$. Thus, high carbon dioxide levels and high acidity (low pH values) tended to coincide, notwithstanding the earlier discussion about equation 1 and the possibility that soil pH measurements may be more relevant than soil CO₂ data.

Soil pH is often closely related to soil calcium carbonate content. In addition, the position of detectable calcium carbonate in the soil profile also marks the position of the weathering front in the soil. It will, therefore, also be useful to compare the data on pH with data on calcium carbonate. The method used is described in Appendix 6, and the data are shown in Fig. 10. Again, gross differences between the sites are clear but the detailed patterns are complex. Darnbrook values are frequently below 20°_{0} to 40-50 cm soil depth, but with maximum values to 30°_{0} . In many cases there is an increase with depth, though this is not so for 2 of the 8 profiles. At Cowside, values rise to $60-80^{\circ}_{0}$ below 40-50 cm with 3 cases out of 4 falling towards zero near the surface, but with one site (at the slope foot) maintaining values of $40-60^{\circ}_{0}$ throughout the profile. At Cowside, the biggest changes on "weathering front" (location of weatherable limestone) occurs between 25-35 cm, at Darnbrook they are at over 50 cm.

Aggressiveness

Aggressiveness values show that Cowside and Darnbrook values overlap at the lower range (0.1–0.2 pH units) but that higher values (greater weathering potential), above 0.5, are limited to Darnbrook and to 2 slope crest positions at Cowside (Fig. 11). Aggressiveness generally decreases with depth, though at the Darnbrook site (3) (podsolic soil) they remain high (>1.0) throughout the profile.

Buffer capacity

In general, the calcareous earths show little provision of acids, with a rapid progression to alkaline values when the alkali sodium hydroxide (NaOH) is added. For the more acid Darnbrook soils, there is evidence of resistance to alkalisation, that is, evidence of a greater supply of acids; for example at 10 ml NaOH added, the Darnbrook values for 5 cm soil depth are still as low as pH 6.3, 8.2, 5.8 and 5.1; and at 20 cm pH 8.3, 8.2, 8.3



FIG. 8. Soil pH values for study sites; 1. frequency distribution.

and 7.4; whereas for Cowside the corresponding values are pH 8.2, 8.5, at 5 cm and pH 8.7 and 8.7 at 20 cm, except the slope top where they are pH 5.8 and 6.5.

Infiltration capacity

Infiltration capacity is a measure of the minimum rate at which soil can accept water (Appendix 4). There is a wide range of data with no clear differences between the study sites (Table 3). The soils would, in general, appear to be capable of absorbing rainfall intensities of between 12 mm hr^{-1} at the lowest, to 660 mm hr⁻¹ at the highest. Rainfall intensities higher than 10 mm hr^{-1} are confined to infrequent, heavy storms. Thus under most rainfall conditions it can be predicted that throughflow will form the dominant runoff process as the soil will be able to accept the rainfall. Only under the heaviest rainfall will infiltration excess overland flow occur on soils with the lower values.

Weight loss of gypsum spheres

The weight loss of gypsum spheres increases with the amount of water flowing around them (Appendix 5); measurements of weight loss thus provide useful measurements of



Soil pH values for the study sites. 2. Hillslope sections.



Soil profile data on calcium carbonate contents. Eight profiles are plotted, four each from the Darnbrook and Cowside sites. The measurements were made on samples taken at various soil depths (see Appendix 6).



 $\label{eq:Fig.11} Fig. 11.$ Soil aggressiveness data. Aggressiveness = change of pH on addition of calcium carbonate powder (see Appendix 3).

Cowside	Slope Foot	Mid Slope		Slope Top	
		240	360	330	
	150	390	240	180	
	180	300	540	480	
	120	330	660	490	
	390	180	360	300	
	480	300	420	300	
	120	150			
	210	150			
mean	221	255	430	280	
Darnbrook	360	270	570	240	12
	480	540	120	270	240
	570	390	420	360	480
	570	390	150	360	210
		270		450	270
		300		300	180
mean	495	360	315	330	232



\$Fig. 12. Gypsum sphere weight losses, weight loss increasing with amount of water flow.

relative water flow in soils. The mean data (Fig. 12) for Darnbrook show a wide range with losses from around 5% to 70%; at Cowside, the mean losses are in a narrower range of 25-75%. There is overlap of the data between slope foot, mid slope and slope top sites, indicating that there is no clear differentiation over the slope. However, there are trends of change down through the soil profile, especially at the Darnbrook mid slope site where there is a rise in weight loss below 35 cm. Similar trends of increased weight loss with depth are shown at Cowside. Both data sets tend to indicate that the potential for erosion by flowing water will be greatest below 35 cm depth, presumably due to a concentration of lateral throughflow at that depth.

COWSIDE

DARNBROOK



Weathering potential

The data described above indicate that weathering potential is distributed unequally between the sites and also within the sites. The generalised data are combined in Fig. 13. It could be suggested that erosion potential should be at a maximum where the zones of lowest pH value, highest aggressiveness and greatest water flow coincide. However, it is clear that these zones do not necessarily coincide: the soils are often most acid at the surface and the greatest water flow is often at depth. Thus, the relative importance of water flow and acidity can be assessed by establishing whether the greatest erosion actually takes place in the acid surface of the soil or at wetter depths. The position of naturally-occurring limestone fragments relative to patterns of soil acidity and soil water flow must also be borne in mind. At Cowside, the pH-related data suggest that erosion should be at a maximum in the top of the soil profile, while the water flow data suggest it should be at the bottom; the "weathering front" (zone of appreciable calcium carbonate) is in the centre of the profile. At Darnbrook, aggressiveness is high throughout the profile, but highest at the top; water flow is greatest at the base and the weathering front is also at the base.

LIMESTONE WEATHERING

Weight loss of limestone tablets

Weight loss of limestone tablets can be used to indicate weathering potential. The tablets are inserted in the soil after weighing. At a later date the high values of weight loss can be used to indicate high weathering potential.

Major differences exist between the data ranges of the two sites, as shown in Fig. 14. The detailed patterns, however, (Fig. 15) show great variability down the profile,



Frequency distributions of limestone weight losses.

especially at Darnbrook. With respect to the two aspects of weathering potential mentioned above, acidity and water flow, it can be suggested that there are often two zones of greatest weight loss: near the surface where organic matter and acidity are highest and again at some depth where greater water flow occurs. Darnbrook site 1, and some of site 2, and Cowside 2 all show high surface values where aggressiveness is focussed, but show decreases with depth because, despite higher water flow, free calcium carbonate exists which can use up weathering potential. At Darnbrook 3, with little free calcium carbonate in the soil and a completely acid profile, weight loss increases with depth where water flow also increases. It is suggested that in acid soils, water flow rate is the limiting factor, with erosion increasing with water flow. By contrast, in non-acid soils, calcium carbonate levels are the limiting factor, with erosion rate increasing with decreasing CaCO₃ levels, irrespective of water flow rates.

Systematic trends of erosion rate with pH are visible on a profile basis (Fig. 16). There is a high degree of dispersion when the data are plotted on a generalised graph (Fig. 17), except that the highest erosional weight losses are below pH 5.5—however, similar pH values also show low weight loss values. High pH values give low weight losses. However, it is the rates at the weathering front which are important (rather than the rates within the





Plot of soil pH and weight loss data; the Cowside data all fall within the shaded zone.



A model of weathering under acid and calcareous soils (adapted from Curtis, Courtney and Trudgill, 1976).

acid soil) where there is no $CaCO_3$ and which are therefore bound to be high. Taking these weathering front data, it is clear that those at Darnbrook are higher, at 0.05–0.3 g a^{-1} , than Cowside, at 0.01–0.02 g a^{-1} , indicating that a higher weathering potential accrues in the deeper, acid, Darnbrook soil profile (as suggested in Fig. 18).

This conclusion means that it may be possible to map the spatial distribution of weathering environments using soil types differentiated by the depth of acidity in the profile. Acid soils tend to exist in the area where there is deeper, acid drift (Bullock, 1971), with shallower, calcareous soils on the screes and on the scar tops. The soils mapped by the present author round Malham Tarn House (Fig. 19) show a more complicated pattern than this, with wet, calcareous soils at the slope foot in some places and a mosaic of rendzinas, pavements and brown earths occurring, according to the depth and the nature of the drift. If the data for erosion rates characteristic of particular soil types are extrapolated from the study sites and compared with the soil map, patterns of erosion in the landscape can be suggested (Fig. 20). This suggests that relief exaggeration will occur, with calcareous scar, scree and draft soil areas remaining upstanding as areas of low erosion. The highest erosion occurs under the acid and podsolic soils.

The question arises concerning the nature of erosion away from a soil cover. In this context, micro-erosion meters (Appendix 7) have been used at a pavement site north of Tarn House. On soil-free surfaces, lichens are powerful agents of weathering (Jones, 1965; Wilson & Jones, 1983) but they may confuse short-term records because of increases in surface height, due to growth, rather than surface lowering. However, long term data (Table 4) give more reliable estimates of surface lowering. The rates range from 0.01–0.07 mm a⁻¹. These compare with those quoted by Clayton (1981, p. 393) of 40 mm 10³ a⁻¹ for surface losses, 40–50 cm in 12,000 years for glacial pedestals and local



Distribution of soils in the Malham Tarn portion of the study area.



Distribution of likely erosion rates over an idealised landscape section.

Table 4. Rates of lowering $(mm \ a^{-1})$ at the subaerial micro-erosion meter site, Malham Tarn Field Centre (adapted from Trudgill et al., 1981). (Positive data influenced by lichen growth omitted). (Data calculated from a variety of measurements)

 $\begin{array}{c} 0.012\\ 0.0135\\ 0.014\\ 0.016\\ 0.017\\ 0.020\\ 0.041\\ 0.055\\ 0.061\\ 0.074\\ \end{array}$

mean 0.0324

high rates of $3 \text{ m } 10^3 \text{ a}^{-1}$ which can be converted to $0.04 \text{ mm } \text{a}^{-1}$, 0.033-0.042 and $3 \text{ mm } \text{a}^{-1}$ respectively, the latter where water draining acid peat runs over limestone. It is difficult to compare these figures directly with weight-loss data, but losses in g a⁻¹ can be converted into an equivalent loss in mm a⁻¹ if the density of the material is known and the weight loss is distributed over the surface area of the tablet (Trudgill, 1975, 1983).

For Cowside, the rates range from $0.02-0.04 \text{ mm a}^{-1}$ at the weathering front; and at Darnbrook from $0.1-0.6 \text{ mm a}^{-1}$, making the calcareous soil rates less than (or just equivalent to) the subaerial rates and the acid soil rates an order of magnitude greater than the subaerial rates. This suggests that differential erosion in the landscape may result from the relative order of rates of rapid erosion beneath acid soil covers, with slow erosion subaerially and in calcareous soils if an acid surface horizon exists.

Solute levels in runoff

Analysis of calcium levels in runoff waters can be carried out by the use of EDTA titrations (Appendix 8). This can give an indication of how far the process of limestone dissolution has evolved, according to equation (1), (page 211). As noted by Clayton (1981, p. 393), the limestone drainage waters are generally low in calcium because of well developed flow-through systems, giving little opportunity for acid waters to react with cave walls. However, this is not true for waters draining from all soils and soil-bedrock contact zones. In some cases, calcium levels are much higher, in accord with the proposition that much karst erosion is concentrated in the soil-bedrock zone (see Table 1). These high levels may then become diluted when they mix with rapidly flowing conduit waters. Thus, analyses of a variety of limestone waters will illustrate the nature and distribution of limestone dissolution processes, especially in terms of the contrast between high calcium levels in the slow percolation, soil/bedrock water and the low calcium level, rapid conduit flow water.

Commonly encountered ranges for selected sites in the Malham area are shown in Fig. 21. The data presented show the ranges which have been found over several years of sampling from the Field Centre. The first three sampling points reveal a contrast in the source areas for water-Smelt Mills Sinks water is derived from an area of calcareous drift, mixed with some acid material and it has a slightly lower minimum value than Goredale Head water which is derived from dominantly calcareous drift; both sites have a mixture of surface water and percolation water contributions, the former especially in wet weather. At Great Close Springs, however, the source is entirely of percolation water, undiluted by overland flow or any surface water, with slow seepage giving opportunity for the pick-up of soil carbon dioxide initially and then for subsequent carbonate dissolution. Here, therefore, the amounts in solution are much higher than for the previous two sites. In other source areas, not shown on Fig. 21, there again a contrast between the solute levels in relation to soils in the source areas; Darnbrook, for example (Fig. 5), has dominantly acid, millstone grit soils, mixed with some limestone drift and has a usual range of 10–50 mg l^{-1} calcium. Cowside, by contrast, drains a dominantly limestone drift area with a high percolation water content, and the range there is usually 70-100 mg l^{-1} calcium. Downstream changes also occur, mostly in relation to losses of calcium by degassing of carbon dioxide, reversing the process shown in equation 1.

Thus, solute levels can be interpreted in terms of the availability of calcium carbonate in the source area in relation to flow patterns. Acid systems tend to be characterised by runoff from upper, peaty areas and the consequent excavation of fast-flowing conduits where there is little time for solute pick up; calcareous areas are characterised more by slower flowing systems. This is because conduits are not so readily excavated by calcareous water. In turn, solute pick up is enhanced because of diffuse, slow flow in carbonate-rich material.



Calcium contents in runoff waters, Malham Tarn area. Data are the commonly encountered ranges in $Ca^{2+} mg l^{-1}$; to convert to $mg l^{-1} CaCO_3$ divide by 0.4.

DISCUSSION

While the data presented above show that erosion rates are, as expected, greater under acid soils, there are a number of important other considerations within this general pattern. There is also the apparent paradox to consider that the greatest erosion (tablet weight loss) occurs under acid soils while the greatest solute levels in runoff (EDTA titrations) occur from areas under calcareous soils. The first consideration concerns the location of the weathering front in soils. This can be defined as a rise in calcium carbonate levels down the soil profile and it is at the transition between the upper acid soil and the lower carbonate-rich zone that most weathering will be focussed. For some carbonaterich soils, calcium carbonate is present throughout the profile and at the soil surface and the weathering potential is supplied by rainfall charged with carbon dioxide and a limited amount of organic acid from humus. Some soil carbon dioxide will also be picked up in the soil profile. Under such a regime, weathering rates are low because there is little weathering potential. However, runoff solute levels are high because of the ample opportunity for weathering to take place in slow diffuse flow through finely divided carbonate material with abundant reactive surfaces. Where the upper soil horizons are carbonate free, extra weathering potential is gained from surface organic horizons which tend to accumulate in more acid soils where soil faunal activity, and hence decomposition, is less. The interest lies in the fact that pH levels at the weathering front are similar (pH 6–7), irrespective of acidity levels in the upper soil and the depth of the acid horizon. However, tablet weight loss rates are not related to the pH of the soil just above the weathering front (Fig. 15). However, they are related to the acidity of the upper profile and especially to the depth of acid soil: the greater the acidity and the greater the depth of acid soil, the greater is the erosion rate. It can, therefore, be concluded that the important factor in influencing weathering potential is the depth of acid soil because as this increases, the greater the pick-up of acids will be in percolating water and consequently the greater will be its aggressiveness. It is thus the balance of supplies which is important: under acid soils, the supply of acids (as measured by buffer capacity and aggressiveness) is high but the supplies of calcium carbonate are low; thus any calcium carbonate present is rapidly dissolved. In more calcareous soils, the supply of calcium carbonate is so great that any weathering potential is rapidly used up, precluding further weathering. It is thus the sequence of events which is important, and the key factors are, firstly, the degree to which weathering potential is picked up (increasing with depth of acid soil) and then, secondly, the degree to which this potential is used up on subsequent contact with calcium carbonate. In addition, under acid soils, subsurface conduits are more likely to open up as the weathering potential is less liable to have been used up in the soil profile, encouraging rapid flow which discourages solute pickup, leading to lower solute levels in runoff from acid soils. This is further encouraged by the fact that under acid conditions, humus decays less giving rise to a thicker mat of humus with a low infiltration capacity. This discourages infiltration and encourages overland flow, with little opportunity for solute pickup, again helping to dilute runoff from acid soil areas. In calcareous soils this does not occur and diffuse flow is encouraged. This encourages higher solute levels to occur, despite lower soil erosion rates because of lack of acids. These factors are summarised in Fig. 22. It is thus clear that the presence of different soil covers can have a marked influence upon the erosion regime on limestone and thus also on the future evolution of the landscape.

The significance of present day modification of the landscape can be assessed by the study of rates of downcutting in the past. Evidence for the latter comes from the work on



the dating of calcite deposits in caves by the Uranium–Thorium method (Atkinson et al., 1978; Trudgill, 1985, Ch 5). Many high level, abandoned cave passages are found in Yorkshire, in which former streams drained to valley floor levels now well above the present one. By dating deposits in the cave-deposits which could not have formed while the cave was still active—the date of abandonment of the cave by streams can be assessed. Rates of downcutting can be obtained by comparing dates with levels; the vertical distance between dated cave levels indicating the rate of downcutting. In the Ingleborough district, to the west of Malham, cave levels at up to nearly 100 m above present levels are indicated at around 350,000 years BP (Before Present), with an intermediate stage some 50 m above present level at 250,000 years BP. An overall erosion rate from the upper level to the present one is equivalent to 0.12 mm a^{-1} . However, it is likely that the valley was greatly deepened during glacial erosion and if the incision was confined to glacial epochs alone, the rate for those periods alone would be equivalent to 0.21 mm s^{-1} . Much of the valley system was established prior to glaciation, with deepening of the valleys by as much as a third again during glaciation. It is unsound to compare rates derived from long-term cave date indices with those of short term weight loss data, the latter being susceptible to short term climatic fluctuations and measurement errors (Trudgill, 1977b; Gascoyne et al., 1983). Moreover, the cave level dating method gives results for channel entrenchment rates while other methods give data for rates beneath soils. However, in their review of dates in Yorkshire, Gascoyne et al. (1983) conclude that rates in cave floors and those under soils are often similar. Certainly the short term rates under acid soils $(0.1-0.6 \text{ mm a}^{-1})$ bracket the rates of $0.12-0.21 \text{ mm a}^{-1}$ given above. Extrapolation of short term data is, however, a risky procedure. What seems certain, is that the patterns of landforms in the area were established prior to glaciation; glaciation then deepened river valleys, formed limestone pavements and left drift deposits over wide areas. It is now the characteristics of these drifts which are the main influence on current landforming processes, with the most rapid rates of erosion occurring under acid soils. The distribution of soils in the landscape thus has a marked influence on differential erosion and the futher evolution of landforms.

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Glossary

 \mathbf{a}^{-1} per annum. $10^3 \mathbf{a}^{-1}$ per thousand years

- Acid an acid is a substance capable of producing hydrogen ions (H⁺) on *dissociation* (qv) in water. A hydrogen ion is a proton and so an acid as a proton donor; a base is a proton acceptor.
- **Aggressiveness** the ability of water to dissolve further mineral material, usually with reference to limestone; see Appendix 3.
- **Bioclastic limestone** one composed of fragments (clasts) of broken biogenic material produced by living organisms (e.g. shells and corals).

Biogenic made by living organisms.

Biomicrite fragments of biogenic origin in a micrite (qv) matrix.

Biosparite fragments of biogenic origin in a *sparite* (qv) matrix.

Brown Earth a soil with a simple horizon sequence: A (mixed mineral-organic), B (weathered mineral material) and C (unweathered parent material), with no other distinguishing features.

Calcareous rich in calcium carbonate.

Carboniferous the geological time span from 350 to 270 million years ago.

Clint an upstanding limestone block separated from the next block by weathered out joint planes termed *grikes* (qv).

Crinoid ossicles circular segments from the stems of crinoids (sea lilies).

Degassing loss of carbon dioxide from solution in water, often in association with the passage from a confined area where water is in contact with air having a high carbon dioxide (CO_2) content to a more open area in contact with air with a lower CO, content.

Dissociation splitting up of a chemical substance into its constituent ions in water.

Dissolution the process of dissolving a solid in a solvent; the solid then becomes known as a *Solute*. See also *Solution*.

Drift deposited unconsolidated material, including glacial material deposited directly but also some reworked material moving downslope (see also *Head*, *Solifluction*).

Foraminifera a group of shell-making protozoan animals.

Gley a soil where all or much of the iron present is in the pale coloured reduced (Iron II) form as a result of waterlogged (anaerobic) conditions; oxidized iron (Iron III) is often also present as red mottles where oxygen in air or oxygenated water can penetrate the soil.

Grike (**Gryke**) the opened joint faces surrounding a *Clint* (qv) on a *limestone pavement* (qv).

Head soliflucted (qv) material moved downslope under Periglacial (qv) conditions.

Horizon horizontal layer of soil material differing in some way from adjacent layer(s).

Humus decomposing plant and animal remains.

Impermeable unable to transmit water.

Karst (karstic) assemblage of landforms characteristic of limestone scenery.

Limestone pavement flat rock surfaces produced by glaciation and often with joints opened by weathering *Grikes* (qv) with *Clints* (qv) between.

Mesotrophic moderately nutrient rich.

Micritic limestone, Micrite (pronounced mick-rite) a limestone composed of very fine (about 0.1 mm or less) calcite crystals originally deposited as a fine ooze or mud.

Misfit (streams) a stream smaller than the valley it currently occupies, where the valley was probably formed by a larger river or different erosion agency.

Moraine a landscape feature produced by the direct deposition of glacial drift.

Mull well decomposed humus (qv), high in calcium; soft and friable to handle.

Ordovician a geological time span from 500-440 million years ago.

pH acidity or alkalinity, defined as the negative logarithm to the base 10 of the hydrogen ion concentration: $pH = -\log_{10} [H^+]$, (see also *Acid*).

Parent material the material which constitutes the basis of soil formation.

Pavement see Limestone pavement.

Percolation water water which moves slowly and diffusely through soil and rock.

Periglacial conditions around ("peri") glacial areas, characterised by freezing and thawing.

Podsol (**Podzol**) a soil with a bleached, leached horizon present under dark humus surface horizons—organic acids are produced in the humus and are responsible for moving iron from the bleached layer to lower, redder layers.

Ranker a raw, acid humus soil present directly over bedrock.

Rendzina a thin limestone soil, often with a mixed profile of organic matter and limestone fragments; the humus is well decomposed (as contrasted with a *Ranker*, qv).

Scar The term given to a short vertical rock face, often present above or below a rock bench.

Scree a slope of fragmented rock particles.

Silurian the geological time span from 440-400 million years ago.

Solifluction the movement of soil downslope under the influence of freezing and thawing, mostly mobile when just thawed and wet and dominantly under *Periglacial* conditions (qv).

Solute a solid dissolved in a liquid, the solvent.

Solution the noun for the aqueous (watery) medium in which the process of *Dissolution* (qv) occurs. Dissolution is the verb for the process, though solution is often wrongly used in the verbal sense. "Solution

processes" refers to processes in solution not the process of solution; dissolution refers to the act of dissolving.

Sparry limestone, Sparite composed of large (up to 1 mm long) crystals of calcite spar.

Throughflow flow of water laterally downslope through the soil.

Weathering front zone of maximum weathering activity, usually with acid soil above and with weatherable minerals below.

APPENDIX 1: SELECTED SOIL PROFILES

COWSIDE (Calcareous slopes)

Rendzina (transitional form to Brown Earth)

Locality: Cowside SD 890693 Upper mid-slope site

Altitude: 358 m

Slope and aspect: 27° NW

Dominant vegetation: Festuca ovina (sheeps fescue), Sesleria albicans (= S. caerulea) (blue moor grass), Carex flacca (glaucous sedge), and Carex panicea (carnation sedge)

0-20 cm A: Very dark greyish brown (10YR 3/2) sandy clay loam with fine to medium crumb structure. pH 7.7. Humose and stony with small angular to subangular fragments of limestone.

20-30 cm B/C: Light brown (10YR 5/4) sandy loam. pH 7.9. Stony with angular-very angular fragments of limestone and a matrix with medium crumb structure

Brown Earth

Locality: Cowside SD 890693-slope-top site

Altitude: 362 m

Slope and aspect: 9.5° NW

Dominant vegetation: Festuca ovina (sheep's fescue), Agrostis capillaris (=A. tenuis) (common bent), and Koeleria macrantha (crested hair grass).

0-12 cm A: Dark brown (10YR 3/3) sandy clay loam. Fine to medium granular grading into subangular blocky structure. pH 5.1. Slightly stony with sub-angular limestone fragments.

12-30 cm B: Dark yellowish brown (10YR 3/4) sandy clay loam with medium sub-angular blocky structure. pH 6.2. Stony—with sub-angular to angular limestone fragments.

30 cm+: Angular head deposits—Great Scar limestone fragments with occasional sandstone erratics. Stony to stone/rock dominant matrix pH 7.8.

DARNBROOK (Acid slopes)

Brown Earth

Locality: Darnbrook SD 895711 just below slope crest.

Altitude: 270 m.

Slope and aspect: 22.5° SW.

Dominant vegetation: Festuca ovina, Anthoxanthum odoratum, (sweet vernal grass), Agrostis capillaris.

0-20 cm A: very dark grey (10YR 3/1) silt-silty clay loam with fine to medium crumb structure. Very strong with subangular fragments (especially sandstone) up to 20 cms in diameter. pH 5.5.

20-65 cm B: Brown-dark brown (10YR 4/3) sandy clay. Weak subangular blocky to medium prismatic structures. Stony with sub-angular fragments 5-10 cms in diameter. Average pH 7.5.

65 cm + C: Variable till and rubbly head, with high percentage of sandstone fragments.

Podsolised Brown Earth (Brown Podsolic Soil)

Locality: Darnbrook SD 895710 Upper mid-slope

Altitude: 365 m.

Slope and aspect: 32° SW

Dominant vegetation: Nardus stricta and Festuca spp. with some Agrostis capillaris.

0-5 cm Ah: Black (10YR 2/1) humose sandy loam with bleached quartz grains and abundant bracken rhizomes.

- 5-9 cm Eg: Very dark grey (10YR 3.1) sandy clay loam with small ochreous mottles. Medium crumb to subangular blocky structure very weakly developed.
- 9-40 cm B1: Dark yellowish brown (10YR 4/4) sandy clay loam-weak subangular blocky structure. Bracken rhizomes present.

40-70 cm B2⁺: Brown (10YR 5/3) sandy clay, weak subangular blocky-prismatic structure. Bracken rhizomes present.

Note. There have been changes in the names of soil types. Peaty gleyed podsols have become Stagnopodsols; peaty gleys, stagno-humic gleys; podsolised brown earths, brown podsolic soils; acid brown earths, brown earths; and calcareous brown earths, brown calcareous earths.

APPENDIX 2. PH MEASUREMENT

pH was measured electrometrically, using a spear head electrode, on air dried soils passed through a -0.25ϕ (1.2 mm) sieve and mixed with deionised water to the "sticky point"—a soil paste which just glistens. The sticky point is the minimum amount of water needed to form a paste.

APPENDIX 3. BUFFER CAPACITY

Buffer capacity was measured by bringing the soil to sticky point (see Appendix 2) and placing it in a beaker, under a burette with 0.1 M sodium hydroxide. 0.5 ml of alkali is added to the soil paste which is then stirred and the pH recorded after stirring. pH data can then be plotted against ml alkali added and the longer the resistance to pH change is, with added alkali, the greater are the reserves of acidity in the soil.

Aggressiveness

This is a similar measurement to buffer capacity but it is made more relevant to natural solution processes by the use of powdered calcium carbonate. Both pure calcium carbonate or powdered limestone may be used (Trudgill, 1983, p. 30) but in this study the former was used. A 100 ml water sample was equilibrated with an excess of powder (at least 20–30 g) and the pH measured before and after addition, the final pH being when no discernable drift occurs on the pH meter. Increases in pH indicate a potential for further dissolution to take place, or "aggressiveness": the greater the increase, the greater the aggressiveness. When assessing the aggressiveness of a soil sample, the powder is added to the sample (50 g) at the sticky point.

APPENDIX 4. INFILTRATION

Infiltration was measured using the method of Hills (1970). Water is ponded in a retaining ring and the level of water measured repeatedly. Initial rates of fall are rapid but they decrease and the final rate is taken when at least three readings give the same rate of fall of water level per minute. This gives the rate at which the soil will accept water when equilibriated with the input (Trudgill, 1983, p. 121).

APPENDIX 5. WEIGHT LOSS TABLETS

This method has been discussed in detail by Trudgill (1975); Trudgill, 1983, p. 75, 159; Crabtree and Trudgill (1984*a*, *b*). Gypsum tablets lose weight in accord with amount of water flow and independently of pH. Rock tablets (Trudgill, 1983, p. 75) were of 1 cm diameter local limestone. Weighing accuracy was 0.001 g.

APPENDIX 6. CALCIUM CARBONATE

This was measured using the reaction of 3 molar hydrochloric acid with limestone, giving off gas and leading to weight loss. The method used was as described by Briggs (1977*a*, 114–116 using the formula $(W_2 - W_3) \times 227.2/W_1$, and not the erroneous formula given in the first printing of the book.)

APPENDIX 7. MICRO-EROSION MEASUREMENT

Micro-erosion measurement was effected using a micrometer dial set in a tripod framework which rests on three studs inserted into the rock. Details of the method are given in Trudgill (1983, p. 104) and also by Trudgill *et al.* (1981).

Quantitative analysis of calcium and magnesium in solution by titration with EDTA

Water samples should be analysed within a few hours of collection and transported carefully in sealed polythene bottles (Crabtree *et al.*, 1981). Titration with EDTA is a standard technique for the analysis of Ca^{2+} and Mg^{2+} ions in solution. EDTA (Ethylene-diamine-tetra-acetic acid, in the disodium salt form) forms stable complexes with calcium, and magnesium. The procedure is to titrate two sub-samples from the same water sample, one for calcium and one for calcium + magnesium. This is achieved by adding a strong alkali to the first sub-sample and this has the effect of precipitating the magnesium so that it does not take part in the titration. The figure for magnesium is gained by subtracting that for the calcium from the second titration for calcium and magnesium with no strong alkali.

The calcium titration: potassium hydroxide is added to alkalise the solution and an indicator is added which forms a complex with the free calcium. Upon adding the EDTA the calcium is complexed by the EDTA (which forms a stronger complex than the indicator-calcium complex). Upon losing calcium, the indicator changes colour. When the colour change is complete, the end point has been reached. The amount of EDTA used is noted and the amount of calcium present in the solution is computed from the ratio in which calcium and EDTA combine.

The calcium + magnesium titration is undertaken in a similar way but a mildly alkaline solution is used instead of a strongly alkaline one.

Apparatus and chemicals needed CAUTION: Potassium hydroxide is caustic to the skin. Ammonia causes irritation to eyes and lungs.

100 ml measuring cylinder or pipette
250 ml conical flask
Retort stand with bosshead and clamp
White tile (or white piece of paper)
50 ml burette
0.025 m EDTA (9.306 g 1⁻¹)
Ammonium purpurate (indicator for calcium titration), 0.02 g in 10 ml distilled water
Potassium hydroxide buffer (for calcium titration), 80 g 1⁻¹
Erio-T (indicator for calcium + magnesium titration), 0.02 g in 10 ml alcohol
Buffer (for calcium + magnesium titration), 70 g ammonium chloride in 570 ml concentrated ammonia, made up to 1 litre
Two small beakers
pH paper
Small funnel
500 ml water sample

Procedure

Set up retort stand, clamp and bosshead. Clamp in the burette so that the tip is just above the level of the top of the 250 ml flask. Place a white tile or clean white paper under the flask to help estimation of colour change.

Remove flask from under burette. Fill burette with EDTA, using the small funnel and taking care not to overfill funnel. Check that tap flows freely. Rinse out all glassware with distilled water.

Calcium

Prepare two colour standards

Take approximately 25 ml of the sample in one beaker and sufficient potassium hydroxide buffer to raise pH to pH 14 (use pH papers to check) and enough ammonium purpurate indicator, a few drops, to give a good colour. Repeat this in the other beaker. To one beaker add EDTA until a strong colour change occurs. The sample in the beaker without EDTA should be a reddish purple colour. The one with an excess of EDTA should be pure mauve, without any trace of red. Use these as colour reference points to help decide the end point during the titration.

Titrate the sample

Pour exactly 100 ml of the sample, measured in the measuring cylinder or pipette, into the conical flask. Add potassium hydroxide to pH 14. Add a few drops of indicator to colour. Perform a rough titration first. Note the burette reading and calculate the EDTA used. Prepare another 100 ml sample and add buffer and indicator as above. Note the burette reading (R1). Run in most of the EDTA used last time but approach the end point carefully, adding the last amount of EDTA accurately, drop by drop, and if you are unsure whether the end point has been reached, read the burette before adding the next drop. R2 is the final burette reading at the end point. Calculate:

 $R_2 - R_1 = V_1 (V_1 = ml EDTA used in titrating calcium)$

 $V_1 \times 25 = CaCO_3$ content of water sample in mg $l^{-1} \star$

Magnesium

Prepare two colour standards as for calcium, but using ammonia buffer to pH 10 and a few drops Erio-T indicator. Before the addition of EDTA the solution should be purple; after, it should be a clear cornflower blue.

Perform a rough titration as before and then an accurate one, approaching the end point drop by drop.

Read burette before titration (R3) and after (R4), then calculate:

R4-R3=V2 (ml EDTA used on calcium + magnesium)

V2 - V1 = V3 (ml EDTA used on magnesium)

 $V3 \times 21.1 = MgCO_3$ content of water sample in mg l⁻¹

Note: With very low concentrations of magnesium it is best to take R3, add most of the EDTA amount used in the calcium titration then add buffer and indicator, and complete titration dropwise. The reporting of data on solution concentrations in limestone studies can vary. Some workers use $mg l^{-1} Ca^{2+}$, others $mg l^{-1} CaCO_3$, as above. The latter does not imply that $CaCO_3$ is the solute species present in solution, reporting in $CaCO_3$ units stems from the use of such data in limestone geomorphology in the calculation of denudation estimates. Data may be converted using an appropriate conversion factor:

$$mg l^{-1} Ca^{2+} to CaCO_3 = Ca^{2+} \times 2.497$$

* $mg l^{-1} CaCO to Ca^{2+} = CaCO_3/2.497$

also

 $Ca^{2+}mgl^{-1} \times 0.02495 = mMl^{-1}$

Milli-equivalents (meq) are also reported, where an equivalent is the atomic weight/valency (for calcium = 40/2) and which has relevance in calculations of balances of ion species and how they combine,

 $Ca^{2+} mg l^{-1} \times 0.04990 = meq l^{-1}$

Data may be reported in parts per million (ppm) or mg l^{-1} . The former is mg solute per kg solution; assuming 1 litre solution to weigh 1 kg, for all practical purposes the data in either units are regarded as interchangeable.