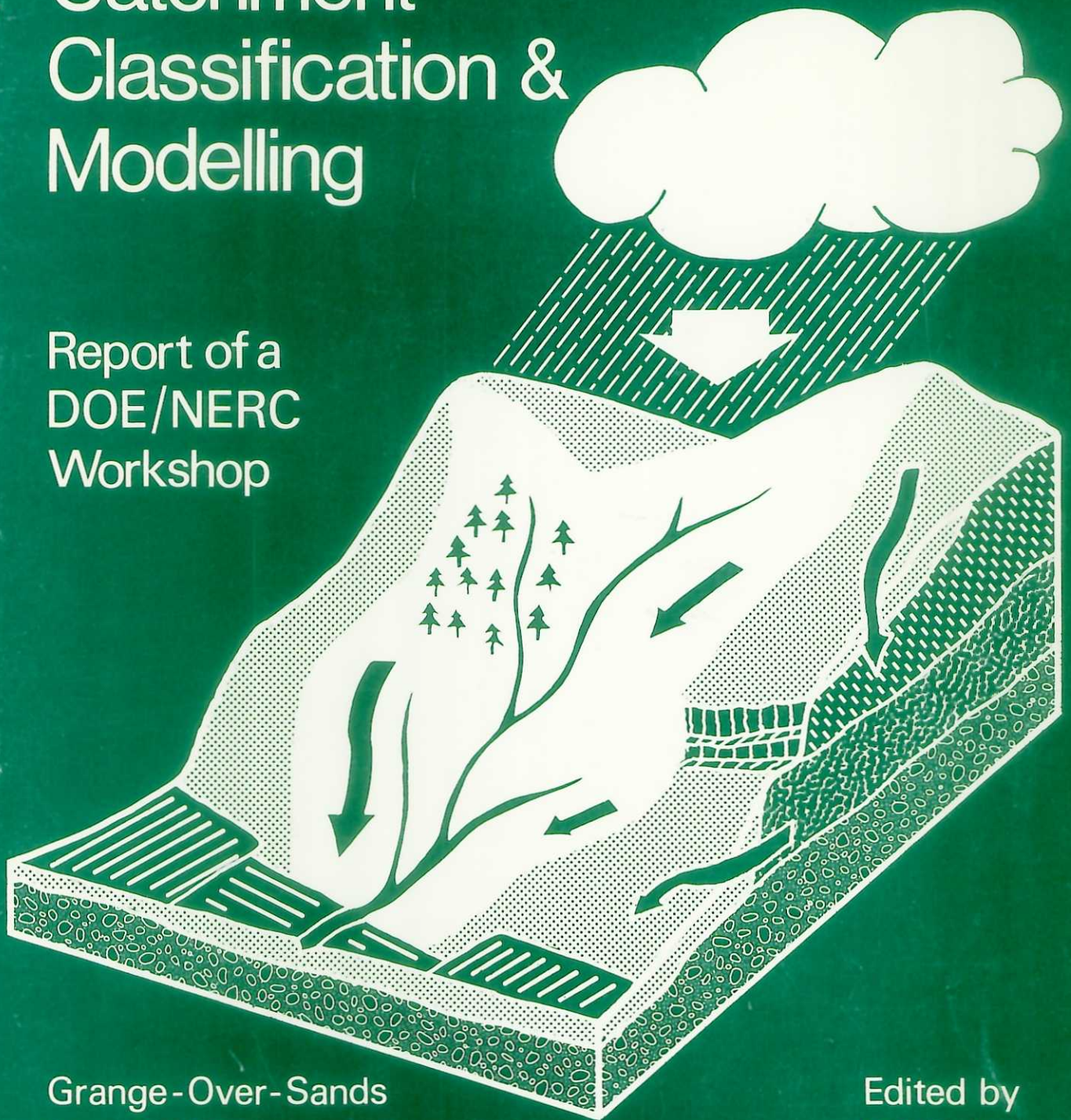


Acidified Catchment Classification & Modelling

Report of a
DOE/NERC
Workshop



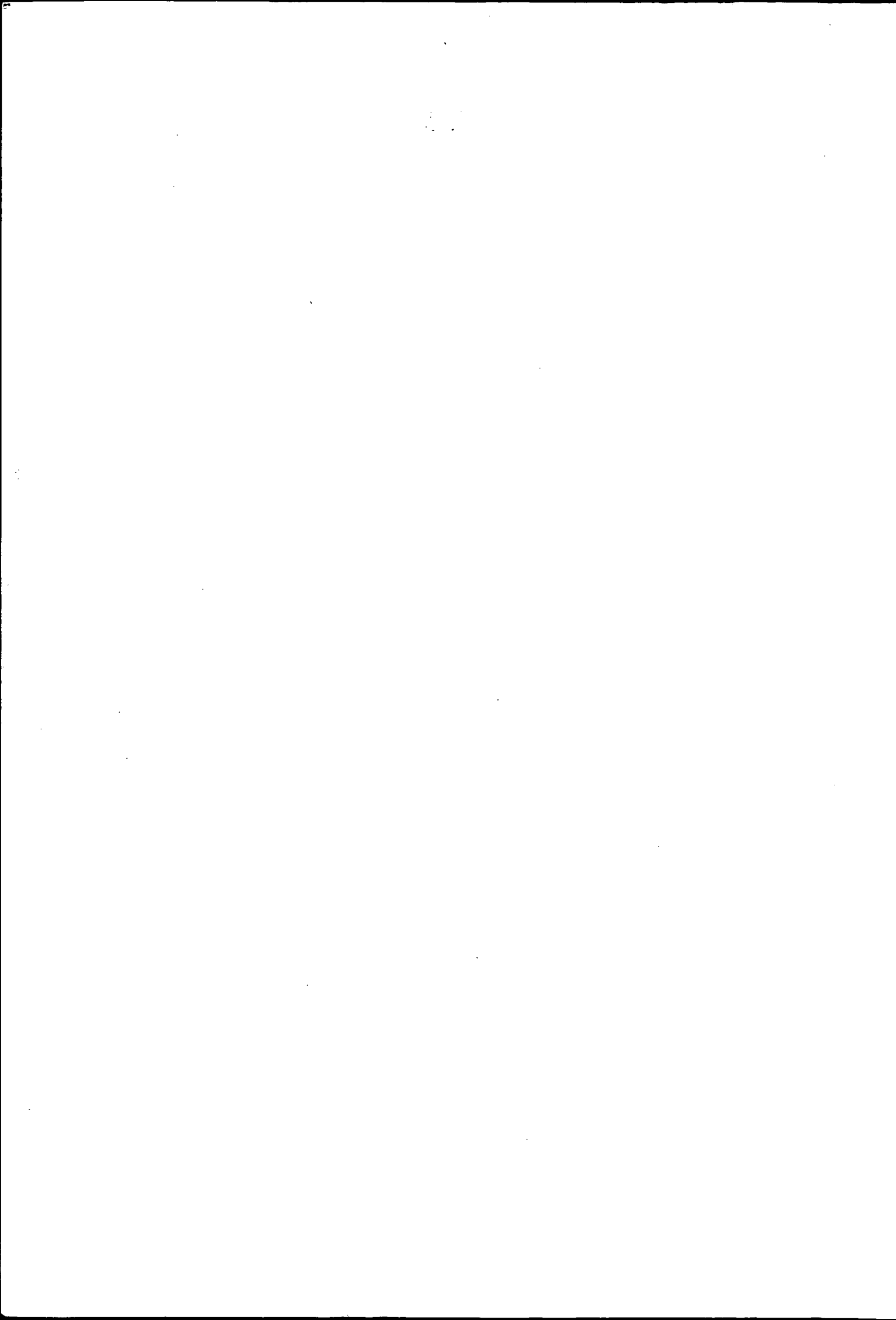
Grange-Over-Sands
March 1986

Edited by
K R Bull

Department
Of The
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Natural
Environment
Research
Council

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DEPARTMENT OF
THE ENVIRONMENT

NATURAL ENVIRONMENT
RESEARCH COUNCIL

**ACIDIFIED CATCHMENT
CLASSIFICATION
AND
MODELLING**

REPORT OF A WORKSHOP HELD AT GRANGE OVER SANDS
18-20 MARCH 1986

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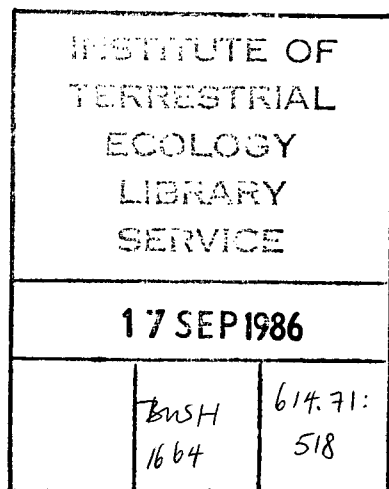
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Introduction

R B Wilson

Over the past few years both the Natural Environmental Research Council and the Department of Environment have devoted considerable funding to studies of the mechanisms of acidification of surface waters in a number of regions of the United Kingdom and also studies of the effects of this acidification on freshwater biota. In two areas, Llyn Brianne in S Wales and the Rivers Esk and Duddon, Cumbria, joint NERC/DOE integrated research projects are being undertaken in collaboration with the Welsh Water Authority and North West Water Authority respectively.

At the same time, the Central Electricity Generating Board and the Royal Society Surface Water Acidification Programme are also funding similar research work in the UK as are a number of other organisations (see Appendices). Most of these initiatives are now beginning to produce data, much of it on a continuous basis. Consequently, research programme managers in both NERC and DOE considered it appropriate to organise a workshop to see how best this data base could be utilised to further the development of classification systems, to identify susceptible catchments, and models, to predict the response of such catchments to changes in acid input, eg decreased acid deposition, afforestation, deforestation, changing land practices etc.

The overall objective of the DOE acid waters research programme is to elucidate the extent of surface water acidification in the United Kingdom and to quantify the role played by acid deposition in this acidification. Within this, the programme aims to:

- i. provide a framework with which to assess the sensitivity of the hydrological and chemical processes controlling catchment acidity;
- ii. investigate the short term dynamic response and to assess the impact of "acid pulses" or episodes on the aquatic environment;
- iii. assess long term acidification processes and the possibilities of remedial action.

Such studies are of necessity multi-disciplinary and in convening the acidified catchment classification and modelling workshop, the organisers were determined to try to reflect this wide range of disciplines and expertise. Consequently, a series of objectives were defined which it was felt would enable all the participants to make a relevant contribution. These were:-

- (i) to look at links between models and classifications with a view to extending current models to wider areas of the United Kingdom;
- (ii) to relate our understanding of catchments to land management practices;
- (iii) to encourage exchange of ideas and information between scientists;
- (iv) to look at the possible use of models and classification systems as policy tools to evaluate the impact of acid deposition.

After some discussion, the organisers agreed the best way to ensure full participation of all the experts attending the workshop would be to operate it on a matrix basis whereby each problem would be analysed, synthesised and summarised by a fixed number of groups whose constitution would be changed at each phase. The conclusions and recommendations of this workshop therefore represent the distillation of the findings of 54 separate work groups which met over 3 days to address the 3 specific questions given them.

Background Papers

ATMOSPHERIC MODELS AND DATABASES

R G Derwent* & D Fowler

INTRODUCTION

It has been recognised for many years that the atmosphere and precipitation over North West Europe are polluted as a consequence of emissions from the combustion of fossil fuels. Although natural sources of these pollutants are dwarfed in industrialised areas, all are removed by the same atmospheric scavenging processes. Many of these removal mechanisms have only recently been defined and for some of the compounds involved our understanding of the air chemistry and deposition pathways is rudimentary.

The main precursors of acid deposition are sulphur dioxide (SO₂) and nitrogen oxides (NO_x). UK emissions of SO₂ increased to a maximum 10-20 years ago, and have decreased over the last decade due primarily to fuel switching by industry and in the domestic sector and the general recession in British industry. NO_x emissions appeared to reach a maximum 5-10 years ago and are following a slight decline before an anticipated increase over the next ten years or so.

In the application of computer modelling techniques to acid deposition, a number of competitive and sequential processes are set up in mathematical form to study their combined effect. The model results in no sense represent a prediction of what is likely to happen in the atmosphere. They merely represent an attempt to visualise the current state of knowledge based on laboratory studies, field experiments and environmental measurements. Much attention has been directed to the calculation of the pattern of the long-term average dry and wet sulphur deposition across North West Europe and the resulting transboundary sulphur fluxes.

In this review, some of the basic processes as described in acid deposition models are examined from the point of view of characterising inputs to remote catchments. Attention is directed to deposition modelling as a subject, without focussing on any particular model or approach. This short review addresses the future developments in modelling that may be anticipated.

REPRESENTATION OF THE IMPORTANT PROCESSES IN ACID DEPOSITION MODELS

Emissions

The annual SO₂ emissions represent some of the best quantified input to acid deposition models. However annual UK SO₂ emissions are not adequate for serious modelling and some refinement is required. It is important to resolve these emissions by:

- height of emissions,
- spatial distribution,
- time of day, week, month and season,
- the simultaneous presence of other pollutants,
- the contribution from other countries in Europe.

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Broadly speaking, it is straightforward to resolve SO₂ emissions on to a spatial scale of 10-50 km. There would, however, appear to be a limit to the temporal resolution of monthly, for SO₂ emissions.

If we look at the available emissions data for the UK and the rest of Europe other than for SO₂ then we can foresee a number of problems in the way of the development of more sophisticated acid deposition models.

Emissions of NO_x are currently open to considerable question and none of the presently available approaches to their estimation are considered to be entirely satisfactory. Much work concerning the temporal and spatial disaggregation of NO_x emissions across North West Europe is required.

There is a general dearth of information on emissions of the other important pollutants which are believed to take part in the deposition of acidic species. These include ammonia, HCl and hydrocarbons. A significant improvement in the description of these emissions is required before significant progress can be made developing sophisticated acid deposition models.

Atmospheric transport and dispersion

The locations of the downwind areas in an acid deposition model which are influenced by the acidic pollutants, or their precursors, emitted from a single source, or an urban area, are determined by the trajectory of the wind borne material. This is determined by the horizontal wind field over the whole depth of the atmosphere into which the pollutant has spread. The wind field usually exhibits substantial changes with height which, when taken with the general uncertainty associated with the depth of the boundary layer and its internal structure, means that the determination of the effective track taken by the pollution can be difficult to obtain.

The track of pollution can be obtained by a step-by-step process from the observed wind fields. Broadly speaking, the trajectories taken by wind borne material are subject to considerable uncertainty (100 km minimum at best), and are available with a time resolution of typically 6 hours.

It is not enough merely to describe the track of the pollutants but attention must be given to their dispersion throughout the boundary layer depth. The processes by which pollutants are dispersed are exceedingly complex and are usually given the most rudimentary of treatments in acid deposition models. Climatological dispersion parameters are typically employed and they may lead to significant discrepancies under particular meteorological conditions.

Chemical transformation of pollutants within the atmosphere

Atmospheric models of the deposition of acidic species in North West Europe require some form of description of the chemical transformations which convert primary pollutant emissions into the acidic species which are deposited. The rates of these processes must be quantitatively correct in the models if reliable deposition maps are required for pollution of UK origin. This is true for transformation reactions involving both homogeneous gas phase reactions as well as liquid phase reactions.

There is no clear way to validate the model representations of the homogeneous gas phase chemical reactions which control the transformation reactions producing acidic species during both day and night. It remains unclear whether these processes are adequately represented in acid deposition models.

In addition to the gas phase reactions largely involving free radicals such as the hydroxyl (OH) radical, a variety of chemical reactions can occur involving droplets, whether rain or cloud droplets, and these require representation in atmospheric models. The description of rates of liquid phase reactions occurring in the atmosphere requires much detailed information about trace gas concentrations and the behaviour of droplets and air flow through clouds.

Most models employ a crude representation of conversion processes with a single transformation coefficient for each pollutant species. Such crude representations bear little resemblance to reality and so it has not been possible to evaluate the significance of these approximations. We must also conclude that most models do not yet have the power to describe how transformation rates may change in response to any changes in atmospheric concentrations.

Wet and dry removal processes

The concise and accurate representation of wet and dry removal processes in atmospheric models is an important prerequisite for any study of acid deposition. The main processes are usually referred to as precipitation scavenging and dry deposition. Each of these processes has been studied extensively in field and laboratory experiments and through theoretical investigations. However, much remains unknown from the experimental and theoretical viewpoint, furthermore the information is not available uniformly for all the relevant species.

In the present review we are principally concerned with wet removal by rain and snow of SO₂, NO₂, HNO₃, sulphate and nitrate aerosol, HCl and ammonium compounds, and dry deposition of SO₂, NO₂, HNO₃, ozone, NH₃, HCl and aerosols to vegetation, soil and water. The turbulent deposition of cloud and mist represents an additional deposition pathway that is of particular interest in upland catchment studies.

In general terms, dry deposition can be more concisely and accurately represented in acid deposition models than wet deposition because it is a continuous process. It is usually handled as flux of material to the underlying surface of the model using the concept of deposition velocity, v_g , and surface resistances. It is usually straightforward to represent the total resistance to deposition in terms of an aerodynamic resistance and a surface resistance. The aerodynamic resistance can be modelling from micrometeorology of the atmospheric boundary layer provided the condition of horizontal homogeneity is satisfied. The surface resistance depends on the nature of the pollutant and the nature of the underlying surface and its biological activity. An extensive data base is therefore required for acid deposition modelling studies.

Currently most models use fixed and 'typical' values of deposition velocities or surface resistances for large areas of the model domain. These values and current knowledge are probably adequate to describe dry deposition on the regional scale with yearly time resolution. However, if dry deposition is required on much smaller distance scales to a specific

crop species or resolve individual catchments, then much more detailed modelling will be required. In particular, the models will have to treat the variation of dry deposition rates for a range of pollutants with vegetation type, time of day and the influence of plant or forest wetness and snow cover. Furthermore, there are a whole range of small scale effects to be considered such as topography, mountain-valley flows and land-sea contrasts that may also be relevant in particular catchment areas.

Whereas direct uptake at the surface by dry deposition is a process which is continuous in time, precipitation scavenging occurs only intermittently in connection with precipitation events. To describe and model the process of precipitation scavenging, it is therefore necessary to take into account not only the physical processes responsible for the uptake of pollutants into rain, cloud, fog or mist droplet and the possible chemical transformation occurring inside it, but also the frequency with which an air parcel finds itself in contact with these droplets.

For pollutants such as sulphate aerosol, nitrate aerosol and HNO_3 , the wet deposition patterns in acid deposition models are largely determined by the average length of dry periods. This is because dry periods are considerably longer than wet periods and scavenging is rapid under wet conditions. It is often simplest then in models, not to consider wet periods explicitly, but use the assumption of complete wet removal of sulphate aerosol, nitrate aerosol and HNO_3 into rain as an upper limit for the wet deposition at each location.

Whilst such crude descriptions of wet deposition are adequate for illustrative model calculations on the continental and national scales, they remain quite inadequate for the estimation of deposition on a smaller spatial scale or during particular pollution events. If deposition patterns on these spatial scales are required, then further detailed knowledge will be required of the following:

- statistics of cloud volumes,
- quantity of air passing through clouds,
- chemical composition of cloud droplets,
- changes of chemical composition in clouds,
- fractions of cloud water removed by precipitation,
- fractions of cloud water evaporating.

There is currently not enough data to represent adequately in acid deposition models, the deposition of acidic pollutants in fog and mist. Cloud and mist are readily deposited on vegetation, particularly coniferous forestation at high altitudes. Wet deposition could be considerably underestimated in upland regions by models due to the neglect of fog and mist processes.

FUTURE MODELLING ACTIVITIES

Whilst the current generation of acid deposition models have been most influential in developing our understanding of the nature of the processes which control the long range transboundary transport and deposition of sulphur compounds, they are necessarily highly simplified representations of the real world. In the manipulation of the basic equations describing acid deposition, a number of assumptions have been made to reduce the complexity, dimensionality and time dependence of the working equations in the different models. Insufficient attention has so far been given to the physical basis behind many of these assumptions and further basic research is needed to resolve many of the present uncertainties.

The long term transport and deposition models have recently been extended to include oxides of nitrogen and hence nitrate in rain and aerosol nitrate. There is a reasonable prospect that ammonia can be included into the models as a source gas and hence ammonium in rain and aerosol can be dealt with. If HCl can be added then it should be possible to calculate most of the major ionic inputs to deposition, including net acidity.

In the long term, the aim must be to reduce the extent of spatial and temporal averaging in the models of sulphur and nitrogen deposition. This will require:

- formulation of more sophisticated models without the need for excessive parameterisations and simplifications,
- attention to the spatial and temporal averaging in all the relevant processes including emissions, transport, dispersion, transformation and deposition,
- attention to the chemical and photochemical, gas phase and liquid phase interactions between pollutant emissions and natural atmospheric constituents,
- attention to the detail nature of catchment deposition processes involving dry deposition, wet deposition and occult deposition.

ACKNOWLEDGEMENT

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DATA REQUIREMENTS AND AVAILABLE DATA BASES ON SOILS AND GEOLOGY

M Hornung & W M Edmunds

INTRODUCTION

Soils and geology are two of the most important variables influencing drainage water chemistry. As such, they are essential considerations in the development of classifications or models of catchment systems. The following paper attempts to identify those properties of soils and rocks which influence drainage water chemistry and which, therefore, should be considered when defining the inputs to classifications or models. The data bases created by the Soil Surveys of England and Wales, and of Scotland, and by the British Geological Survey are then summarised. Finally, the data requirements for specific purposes are assessed and compared with those available from the data bases.

DATA REQUIREMENTS

For the purpose of this review only data published, or held by, the British Geological Survey, the Soil Survey of England and Wales, and the Soil Survey of Scotland is considered. Additional data, especially geological, is held in universities, polytechnics and by commercial companies but this is more difficult to assess and evaluate.

Data requirements will be influenced by the aims of a particular study, for example catchment classification, comparison of catchments being utilised in processes studies, development or application of hydrochemical models. The level of resolution in the data which is required will also be influenced by, for example, the size of the smallest catchment being classified, or the level of accuracy demanded in the output from a model. Whatever the purpose or scale of the study, however, the soil and geological data requirement concerns those properties of soils, drifts and bedrock which will influence drainage water chemistry, in particular:

- the chemical reactions between water and soil/drift/bedrock
- the water pathways from surface to stream
- the residence/contact time of waters in the soil/drift/bedrock

Soils

The soil-water reactions which influence the chemistry of waters held within, and moving through soils have been discussed by Bache (1981, 1983, 1984), Wiklander (1974) and Johnson & Reuss (1984) and Mason & Seip (1985). The reactions involved include:

- solution - precipitation (particularly solution of carbonates and organic acids)
- ion exchange
- silicate weathering
- anion adsorption - desorption (particularly of SO_4)
- oxidation - reduction (particularly oxidation of sulphides and organic forms of S and N)

Soil properties which relate to, and provide information on these processes include:

pH
organic matter content
carbonate content
content of exchangeable cations (including Al)
cation exchange capacity
base saturation
exchangeable acidity
SO₄ and NO₃ adsorption capacity
buffering capacity
redox potential
content of weatherable minerals

Some of these parameters are important because of their influence on short-term soil-water reactions, others such as the content of weatherable minerals, will influence reactions over the longer term.

Water pathways through soils are influenced by porosity and permeability of the soil materials, in particular, by vertical and horizontal changes in permeability (McCaig, 1985). Direct measures of porosity and permeability can be made but soil parameters which influence them, and which are usually recorded, are:

the presence or absence of cementation, compaction or induration
texture
organic matter content
soil structure
presence or absence of soil pipes
bulk density

Residence time is also influenced by texture, structure, porosity and pore size distribution, the degree of saturation and the presence of features such as soil pipes.

Both chemical and physical properties change vertically, between soil horizons, and data on each horizon is, therefore, required. These properties also vary between soils; as catchments almost always contain several soil types, data are required on each type.

Drift deposits

Drift deposits may either be formed from locally derived materials (autochthonous drift) or from materials transported over long distances (allochthonous drift). Examples of the latter include glacial tills and moraine deposits, and may include a complex mixture of different parent lithologies having different susceptibilities to weathering. The properties of drift materials which influence water-rock reactions, water pathways and residence time are similar to those for soils. Thus, data is required on carbonate contents, amounts of readily weathered minerals, presence or absence of sulphide minerals, texture, porosity, permeability and thickness, plus information on the vertical and lateral variation of these parameters within the drift mass. There is often a correlation between these properties and the rocks from which the drift was derived especially in the case of autochthonous drifts, and the mode of deposition. Where soil survey information is available, this can be combined with that available from the Geological Survey to provide improved data on drift deposits.

Bedrock

The processes influencing reactions between bedrock and percolating waters have been discussed by Drever (1982), Mason & Seip (1985), and Edmunds &

Kinniburgh (1986); the most important processes are:

- mineral dissolution and precipitation (especially carbonates and silicates)
- hydrolysis of silicate minerals
- redox reactions

The principal mineral groups involved in these reactions are carbonates, alumino-silicates and sulphides. Solution of carbonates (calcite, dolomite, siderite) and alumino-silicates (feldspars, micas, pyroxenes, amphiboles and olivines, especially) will buffer acidity in percolating waters while oxidation of sulphides can give rise to increased acidity. In general, there is a broad correlation between rock type and mineral content. Thus, basic igneous rocks contain a larger percentage of readily weathered silicates than acid igneous rocks, most grits and many sandstones are poor in both carbonates and weatherable silicates. There can, however, be wide variations in mineralogy and geochemistry within rock types, eg greywacke, shale, granite, schist. A more precise characterisation of these rock types would be needed for detailed studies. Carbonates and sulphides may also be present as secondary vein minerals, and as cements in sedimentary rocks. Small amounts of these minerals can have major influences on drainage water chemistry.

The extent to which reactions take place between the various minerals and percolating waters depends upon water pathways contact areas and residence time. These will be influenced by the primary and secondary porosity and permeability of the rocks, and how these change with depth; in particular, the occurrence of bedding planes, joints, cleavage, fault zones, and the depth of weathering need to be known. There is often a broad correlation of physical characteristics with rock type. Thus, most granites are rather massive, many limestones are well jointed, shales are usually finely bedded; although there will be considerable variation within groups. Detailed studies will however require specific geological data obtained from the study area.

Catchment size will have an important influence on the residence time of groundwaters. In larger catchments deeper groundwater circulation is possible and the pathways of groundwater entering streams will be made up of a combination of deeper water having long residence times and short resident time groundwater taking routes through shallow weathered horizons.

AVAILABLE DATA BASE

Geological data

Maps of solid geology are available for the whole of the UK at scales of 1:2.5 million, 1:1 million, 1:625,000, 1:250,000 and 1:63,360 or 1:50,000 (HMSO, 1985; NERC, 1986). There are, however, no recent surveys of large areas of the Scottish highlands and the Cambrian mountains; the available 1:63,360 or 1:50,000 maps for these areas are based on surveys which, in many cases, were carried out last century. Larger scale maps, at scales of 1:25,000 or 1:10,000 have been published for a few areas of particular geological interest, for example, the Cross Fell Inlier, or areas of economic importance, such as the coalfield areas. The field surveys for the recently surveyed 1:63,360 or 1:50,000 maps, were carried out at scales of c. 1:10,000: maps at this original field survey scale can be consulted at the offices of the Geological Survey. The current availability of British Geological Survey maps has also been summarised by Bain (1986).

The map units for the sedimentary strata on the solid geology maps, are

based mainly on stratigraphic subdivisions but the map legend also provides some information on the main rock type, or types, within these stratigraphic units. The resolution of the map units, and the amount of information provided, on rock type and characteristics, varies with the scale of the map. On the smaller scale maps, the map units may contain several lithologies varying considerably in mineralogy or geochemistry, while other units may be relatively homogeneous. Thus, on the 1:625,000 scale maps, unit 80 "Tournaisian and Visean (Carboniferous Limestone Series)" will include limestones, sandstones and shales; no information on rock type is given on this scale map for Silurian, Ordovician or, on the southern sheet, Cambrian strata. On the 1:63,360 and larger scale maps individual strata may be differentiated down to beds of a few metres in thickness; important stratigraphic marker horizons of <1m thickness may be indicated. For example, on these maps individual limestones, sandstones and shales of the "Carboniferous Limestone Series" are often shown. The legends of these larger scale maps provide more information on rock type; this information can be extrapolated to the units on the smaller scale maps for which lithological information is absent.

Metamorphic and igneous rocks are identified by a combination of geological age and lithology. The level of resolution of the lithological units varies with map scale. Thus, at the smaller scales, the map units usually include several related rock types; "granite, syenite, granophyre and allied types" are grouped together on the 1:625,000 scale map. On the larger scale maps some indication of the type of granite or schist, for example, may be given.

Regional memoirs provide general information on the lithology, mineralogy and chemistry of the rocks within the area covered. The 1:63,360/1:50,000 series sheets also have comprehensive accompanying memoirs. The main focus of the memoirs and reports, however, is stratigraphic with relatively little information on the geochemistry or mineralogy.

Two national maps of drift geology are available at the 1:625,000 scale. These show the Quaternary deposits of the UK, indicating the presence or absence of drift and its mode of origin; the latter provides a general indication of texture. There is, however, no indication of the thickness, chemistry or mineralogy of the drift deposits. If the drift material was derived from adjacent or underlying bedrock (autochthonous drift), then information on chemistry and mineralogy can be inferred from the maps of solid geology. Information on drift geology is overprinted on the 1:63,360 and 1:50,000 maps and 'drift' versions are also available of some of these maps. As with the 1:625,000 maps, these show the distribution of superficial deposits with an indication of their mode of origin, eg alluvium, glacial till, fluvio-glacial deposits, peat. Additional information on the drift deposits may be included in the memoir accompanying the 1:63,360 or 1:50,000 maps but even here there may be little data on thickness, and spatial variation, mineralogy or chemistry.

Two other series of maps which may be useful in catchment studies are the hydrogeological maps published by BGS, at scales of 1:625,000 and 1:50,000 and geochemical atlases and maps. The hydrogeological maps can be used to locate the principal aquifers and the presence of impermeable strata, and to provide a guide to the importance of baseflow and residence times. The Wolfson Geochemical Atlas (Webb 1978) and the Regional Geochemical Maps of the United Kingdom published by BGS (for further details see Plant (1984)), are based on analysis of stream sediment samples collected at, or near, the intersections of 10km grids. They allow the identification of mineralised areas where high levels of heavy metals and related gangue minerals, including calcite, may be expected. It should also be borne in mind that large amounts of unpublished geological data can be accessed via the various

offices of the British Geological Survey.

In addition to the data base produced by the British Geological Survey, very useful accounts of the geology, often with maps, of some regions have been produced by other organisations. Thus, the Yorkshire Geological Society has published, 'The Geology and Mineral Resources of Yorkshire' and 'The Geology of the Lake District'. There also exist a large number of detailed regional geological studies in the open literature.

It is important when using published geological maps to bear in mind the method used in field survey and the limitations imposed by scale. The field geologist can only identify, record and interpret strata exposed at the surface. In areas with extensive drift covers, exposures will be limited and scattered. The subsurface geology is inferred from the surface outcrops. Although the geologist can utilise a powerful array of geophysical, geochemical and remote sensing techniques to support and aid field surveys, small scale, but important, subsurface or subdrift changes may still remain unrecognised. These small changes may have a profound influence on groundwater chemistry; regional information on groundwater and surface water chemistry may, in fact, be the only way of identifying small but important distributions of carbonates and other buffering lithologies or minerals.

Soil data

Maps showing the distribution of soils over the whole of Britain are available at scales of 1:1,000,000 and 1:250,000. Larger scale, definitive maps (1:63,360, 1:50,000 or 1:25,000), based on detailed field surveys, are available for some 30% of the UK and provisional, or reconnaissance surveys at 1:50,000 or 1:25,000 are available for the rest of the UK (Soil Survey of England and Wales, 1984; Soil Survey of Scotland, 1986). The map units and the resolution of the maps varies with scale. The units on the 1:1 million map of England and Wales are based on the dominant soil group and parent material (see footnote); for example, in unit 64 on the 1:1 million soil map of England and Wales the dominant soil group is 'brown podzolic soils' and the parent material is derived from 'granite and associated drift'. The associated soil groups and the characteristics of the dominant and associated soils are also given in the legend. The latter provides a general indication of soil depth, texture, drainage and stone content.

The map units on the 1:250,000 maps of England and Wales differ from those on the maps covering Scotland but both series of maps convey essentially the same type and level of information. The maps for England and Wales are based on soil associations which comprise a group of soil series (the soil series concept is discussed below) based on a given parent material: the association name is based on that of the dominant soil series. The accompanying memoirs provide summarised soil descriptions plus selected analytical data, eg texture, pH, calcium carbonate content, organic matter content. These analytical data are mainly derived from the detailed surveys carried out in support of the definitive, large scale mapping programme. The map units on the 1:250,000 maps of Scotland are also based on soil associations, which are groupings of soils formed on one parent material. Individual map units are sub-divisions of the associations comprising a number of the soils within the associations: the units are, effectively groupings of soil series but series names are not used in the key. The

Footnote: Fuller discussions of the systems of soil classifications used in the UK can be found in Avery (1980), Clayden & Hollis (1984), any of the bulletins which accompany the 1:25,000 scale map of England and Wales, eg Soils and their use in Wales (Rudeforth et al, 1984) and Futty (1986)

memoirs accompanying the maps of Scotland gives a broad indication of the main characteristics of the soils within each map unit: there are no profile descriptions or analytical data.

The larger scale maps (1:63,360, 1:50,000, 1:25,000) are all based on the soil series concept. In Scotland the series are grouped into the larger associations, as used above, but the map unit remains the series. In complex areas, particularly in the uplands, soil complexes, groupings of soil series, are occasionally used. On the 1:25,000 maps the series may be further subdivided into phases on the basis of variations in one soil characteristic, eg depth, or locational features; thus, deep phases or steepland phases of a given series may be recognised. Almost all the definitive large scale maps (1:63,360 and larger) will be based on ground survey at 1:25,000 scale or larger. The original field sheets, or maps at the survey scale, may be available for consultation at the offices of the Soil Surveys. These detailed surveys have been concentrated in lowland, agricultural areas of Britain. Most areas with acid surface water, or waters sensitive to acidification, are, however, in the uplands. The only available large scale maps for much of upland Britain are based on reconnaissance surveys.

It can be seen from the above that the soil series concept is an important one in the survey of, and presentation of information on, soils in the UK. It is also a very powerful concept in that it incorporates a large amount of information. A given soil series comprises soils with a similar sequence of horizons developed in a given type of parent material; for the present discussion this can usefully be approximated as a given soil sub-group as expressed on one soil parent material. The Soil Survey of England and Wales use a combination of three main properties when defining soil series (Clayden & Hollis, 1984); these are, the broad type of the parent material, eg bedrock, gravelly materials, thick till, texture of the soil material, and any distinctive mineralogy. Thus, the Duneswick series comprises typical stagnogley soils developed in clayed glacial till derived from Carboniferous rocks. The Soil Survey of Scotland uses a similar approach, for example, the Darleith series comprises brown forest soils developed in drifts from basaltic lavas or basic intrusive rocks. The difference between the soil series classification unit and the soil series based map unit needs to be stressed. The map unit is dominated by soil profiles which satisfy the concept of the given soil series but it is not a pure unit; in general, 60-80% of the soils within a map unit will belong to the given soil series.

A memoir, or record, accompanies most of the larger scale, definitive maps. This contains detailed profile descriptions (Hodgson, 1974) and analytical data for each soil series. The profile descriptions include information, for each horizon, on, thickness, structure, porosity, pore size distribution presence of impermeable horizons and stone content. The England and Wales memoirs and records include data, for each horizon, on texture, loss on ignition, bulk density, calcium carbonate content, pH, extractable Al, Fe and C, exchangeable base cations (earlier memoirs only) and cation exchange capacity for each horizon of the main soil series within the area covered. The memoirs for Scotland include the same data, except that information on exchangeable cations is always given, plus base saturation and some information on trace element contents.

If a detailed soil survey is available for the area of interest, data for many of the soil parameters discussed in section 1, above, will be available in the accompanying memoir or record, or from the soil surveys' information system. There will not, however, be data on anion adsorption capacity or the presence of soil pipes, and the information on exchangeable cations, buffering capacity, content of weatherable minerals, porosity and pore size

distribution may be limited. Some of these properties, for which there is little data, will, however, be highly correlated with other soil and parent material properties for which data will be available. Thus, anion adsorption capacity will be broadly correlated with parent material type and the levels of readily extractable iron and aluminium, both these will be 'taken into account' within soil series definitions. Cation exchange capacity is highly correlated with texture (in particular, clay content) and organic matter content; soil series based data will include information on these two parameters. Content of readily weatherable minerals will also be related to soil sub-group and parent material type, and, therefore, to soil series. For some purposes, therefore, the soil series may incorporate much of the information required and can be used as a surrogate for the individual parameters.

A national soil inventory will soon be available, from the two soil surveys, based on observations at the intersections of a 5km grid. Profile descriptions were recorded at each intersection and samples were taken for analysis at 10km intersections. The 1:250,000 maps have now been digitised and will soon be available on disc. Profile and analytical data from the detailed field surveys and the national inventory sites can be rapidly accessed through the soil surveys' soil information systems.

The 1:62,500, and larger scale, definitive maps are based on detailed field survey. The 1:250,000 National Soil Map utilised the information from the larger scale, definitive maps plus reconnaissance surveys of the rest of the area. The available 1:1 million map was based on known relationships, derived from the detailed surveys, between soils, geology, relief, altitude and climate. A revised 1:1 million map, based on the National Soil Map, will soon be available.

Two points must be borne in mind when using data from soil maps

- 1 the inherent spatial variability of soils and
- 2 the density of observations, and survey method, used to produce a given map or report.

It was noted above, that in the soil series map unit some 60-80% of the soils usually satisfy the definition of the given soil series; the other 20-40% of the soils are variations from the named series, perhaps, even, satisfying the criteria of another series. Map units are not pure even on the largest scale maps. The records, or memoirs, also contain relatively little information on variation in given soil properties within a series. In detailed studies of small catchments these within series and within mapping unit variations may be important factors. The larger scale, definitive maps in the UK will be based on approximately 1 auger or pit observation per 8 hectare. Reconnaissance, or provisional, maps are based on many fewer field observations. These field observations are, of course, combined with much other information, eg land form, geology, vegetation and land use, to derive the mapped soil boundaries but the density of observations may well be inadequate for detailed catchment studies. The resolution of the map and soil data must be matched to the intended use and, hence requirements.

DATA REQUIREMENTS FOR SPECIFIC PURPOSES V THE SUITABILITY OF AVAILABLE DATA

The properties of soils, drift and bedrock which influence drainage water chemistry were outlined in section 1. If data for all the parameters listed in section 1 were available for each horizon of each soil in the catchment, for the drift and the bedrock, then one would have a data base which would satisfy the requirements of most classification and modelling exercises. Such a comprehensive data set will, however, rarely be available and, for

many purposes may not be required. We now consider the data requirements for a number of specific uses and attempt to evaluate the adequacy of available data bases for these uses.

General, environmentally based classifications

In section 2, it was suggested that the definition of a given soil series incorporated a consideration of many of the soil properties which influence drainage water chemistry. It was also suggested that there is a broad correlation between the properties of bedrock, which influence drainage water chemistry, and rock type. Soil series and rock type provide, therefore, suitable inputs to many general classifications of catchments, acting as integrators and surrogates for the individual parameters. Some grouping of series with similar characteristics will also be possible, and some thought needs to be directed to this by soil scientists. Alternatively, the soil input to a general classification can be separated into soil sub-group, or group (depending on the scale of resolution required), which are indicated on all the series based maps, and parent material. It is important, however, that a consideration of both is incorporated into the classification. Group, or sub-group, alone will not provide information on, for example, content of weatherable minerals or the presence of carbonates at depth in underlying till.

Data on soil series, or associations, and rock types can be taken from published maps. When using map data, however, it is important to be aware of the limitations imposed by the level of resolution of the initial survey data, the nature of the map units and by cartographic limitations. The variation within the soil series map unit and the frequency of observations were mentioned in section 2. Cartographic limitations will determine the smallest area which can be drawn on a given map, for example, the minimum area which can be shown on a 1:250,000 scale map is 150 ha and on a 1:50,000, 6 ha.

In section 1, we noted that the 1:63,300, 1:50,000 and 1:25,000 maps were based on soil series and on detailed field survey. These maps will form a good basis for classification of catchments but the size of the smallest catchment to be classified is an important consideration. As the size of the smallest catchment to be classified decreases, so the significance of small areas of soil not shown on small scale maps, and within series variations will increase. Series based maps at a scale of 1:25,000 are probably adequate for classification of catchments down to 100 ha and 1:50,000/1:63,360 maps for catchments down to 500 ha. Field sheets of areas, with published maps at 1:63,360 or 1:50,000, may exist at 1:25,000 and, if so, could be consulted at the Soil Survey. The major gap in the required data, which does not correlate well with series, is the presence or absence of soil pipes: these seem to be very important features in parts of Wales and northern England. Published soil maps are probably not adequate for classification of catchments < 100 ha. As noted above, inclusions of soils not detected, or not recorded, at the normal level of field survey may be important in these cases: within series variations may also have a significant role. Series based surveys with field survey at a scale of 1:10,000 are probably useful for classifying catchments down to c 50 ha. The catchment sizes given here should only be used as a very general guide as the complexity of soil patterns varies with relief and geology.

Soil information based on detailed field survey is not available for large areas of the uplands, which is where acid waters are concentrated. However, the provisional or reconnaissance maps which are available are almost certainly adequate for classification of catchments > 1000 ha. Where the catchment units being classified are < 10,000 ha the associations and map

units used on the 1:250,000 scale National Soil Map provide an adequate basis for classification.

The large scale geological maps, 1:62,500/1:50,000 based on recent surveys contain sufficiently detailed stratigraphic information and, information on rock types for classification of catchments down to c 500 ha. With progressively larger catchments the data on the 1:250,000 series maps is probably adequate, eg for catchments >10,000 ha, within the limitations mentioned above. Even at this scale, however, the available data for larger areas of the Highlands of Scotland may be barely adequate. For catchments smaller than 500 ha, field sheets at the 1:10,000 scale would be suitable, if available. In the case of most catchments but especially small catchments, < 100 ha, the major problem will be the lack of adequate data on secondary carbonate or sulphide mineralization, or on the nature of the cementing material in sedimentary rocks. In larger catchments the influence of these factors will usually be overridden by other factors.

Information on drift geology is very variable and rarely contains the type of information discussed in section 2. As suggested earlier, an integration of data available from the Soil Surveys and the Geological Survey could provide an improved data base.

Specific classifications - sensitivity to acidification

A number of authors have attempted to classify soils in terms of their susceptibility to acidification, eg McFee (1980), Wang and Coote (1981). The inputs to these classifications are specific soil parameters; the parameters vary between the classifications but usually include some combination of cation exchange capacity, base saturation, pH, organic matter content and texture. Wang and Coote (1981) use a combination of texture class, or clay content, and cation exchange capacity, or pH and classify soils as non-sensitive, moderately sensitive or highly sensitive to acidification (Table 1). All calcareous soils are classified as non-sensitive. The classes used by McFee (1980) are defined on the basis of the impact, on the base saturation of the soils, of 25 years input, at 1000mm per year, of rainfall at pH3.7. The groups are based on the cation exchange capacity of the top 25cm (Table 2), and three classes are used, non-sensitive, slightly sensitive and sensitive. Soils containing free calcium carbonate, or which are subject to frequent flooding are classified as non-sensitive regardless of their cation exchange capacity. The classification of individual soils is seen as the first stage in regional assessments of sensitivity of soils. The second stage is to allocate geographical areas to sensitivity map units, based on the soil classes. McFee (1980) provides guidelines for allocating areas to his map units:

- NS The area contains mostly non-sensitive soils
- SI Sensitive soils dominate the area
- SSI Slightly sensitive soils dominate the area
- S2 Sensitive soils are significant but cover less than 50% of the area
- SS2 Slightly sensitive soils are significant but cover less than 50% of the area.

The information needed for these classifications is available for most of the soil series which have so far been defined in the UK. The soil series could, therefore, be allocated to the various susceptibility classes, using the soil surveys' information systems; for series occurring in England and Wales, the information could be rapidly accessed via the National Catalogue of soils, NATCAT (Jarvis, 1985). Data from classifications of this type could be used as an input to a classification of catchments with respect to

susceptibility to acidification. An exercise of this type has already been carried out for Scottish soils by the Soil Survey of Scotland (Nolan *et al*, 1984). The study was based on the 1:250,000 soil maps. It utilised data on the texture, exchangeable cations, base saturation and pH of the surface horizon of the dominant soil type within each map unit. The general points made above, about the suitability of available data for classification of various sized catchments, will also apply here.

Classification of the map units of the solid geology map (1:625,000) of the UK according to sensitivity to acidification has been provided by Kinniburgh & Edmunds (1984) and Edmunds & Kinniburgh (1986). The classification was developed as part of an assessment of the susceptibility of UK groundwaters to acid deposition. Four classes were recognised (Table 3) ranging from "No likelihood of susceptibility," to "Most areas susceptible to acidification ...". The classes are based on groupings of rock types and the known relationships between rock type and mineralogy and geochemistry. The map units on the susceptibility maps are based on stratigraphic units, but also utilise available information on the dominant rock types within these stratigraphic units. The classes could be used in a classification of catchments on the basis of susceptibility to acidification.

Comparative catchment studies/process studies

Studies such as those comparing moorland and forested catchments, for example, to assess the impact of land use on water chemistry, or detailed process studies, such as those in progress at Plynlimon, Loch Fleet, and Llyn Brianne, require more detailed soil data than available from published sources. Small areas of soils, small variations in soil pattern between catchments and within series variations can have significant influences on streamwater chemistry. Data should be available to allow a quantitative comparison, or assessment, of the soil pattern in the study catchment(s) and to enable the interpretation of processes within the soil. This clearly requires a detailed soil survey and sampling exercise and a wide ranging analysis of the samples. Ideally this should provide information on all the parameters discussed in section 1. In most cases a special survey will have to be commissioned. The intensity of any such survey, and the method used will be influenced by the size of catchments but grid based observations are commonly used. The size of the grid will vary with catchment size. At Plynlimon in mid-Wales, Hornung *et al* (1985) used a 30m grid in catchments ranging from 5 to 10 ha in size. The soils may be classified into series, or phases, or sub-groups; a series-based classification is preferable. The classification must include information on parent material. The grid based survey provides data on within series variation in properties and allows an easy quantitative comparison of catchments. Sampling should be based on the same grid but will not be necessary at each intersection.

Detailed studies also require information on small variations in bedrock and published data may prove inadequate, especially in areas such as the Scottish Highlands and the Cambrian Mountains. Recent field surveys at 1:10,000 scale may be suitable except for the recurrent problems of vein mineralization and nature of cementing minerals. More detail is required on drift deposits than normally recorded. In particular, estimates of thickness, and spatial variation, and depth of decalcification of initially calcareous drift are important.

Hydrochemical simulation models

The data requirements for existing, published models vary considerably from model to model. A full suite of soils and geological data, as outlined in section 1 would, however, satisfy almost all available models. The MAGIC

model developed by Cosby et al (1985) requires data on soil depth, porosity, bulk density, cation exchange capacity, base saturation, maximum sulphate adsorption, exchange of sulphate with water in the soil, hydrogen ion concentration, weathering rates, selectivity coefficients for Al, Ca, Na Mg and K, partial pressure of CO₂. At present, the model considers the dominant soil in the catchment and one horizon, plus overall soil depth. New versions now being developed will incorporate two horizons, a near surface organic or organo-mineral layer and subsoil.

The integrated Lake Watershed Model - ILWAS - (Chen et al, 1985) considers several soil horizons and till layers. The soil inputs required for each horizon include bulk density, saturated hydraulic conductivity, field capacity, permeability, cation exchange capacity, base saturation, cation exchange capacity, selectivity coefficients, anion adsorption coefficients for PO₄, SO₄ and fulvic acid, weathering rates, and percentage by weight and chemical composition of the weatherable minerals.

Ideally, the required soil parameters should be determined for the soils and drifts of the catchment studied. If soil survey data is available for the catchment, there will be information on several of the parameters as part of the normal suite of soil analyses. Several of the parameters for which data is not generally available are highly correlated with other parameters for which data may be available. Thus, Chen et al (1983) give the relationship between field capacity, and soil moisture, and texture class, based on information given by Brady (1974). They also use data from Haugh (1957) and Summers et al (1980) to give relationships between permeability and texture. Values for some parameters can also be taken from published data for other areas. The various models have served to highlight those parameters for which data is not generally available and where more research is required, for example on weathering rates.

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TABLE 1 SOIL SENSITIVITY RATINGS

	Texture	Clay %	CEC (meq. l ⁻¹)	pH
Non-sensitive		All calcareous soils		
	Clayey	>35	25 - 40	>5.0
	Loamy	10 - 35	10 - 25	>5.5
Moderately sensitive	Clayey	>35	25 - 40	4.5 - 5.0
	Loamy	10 - 35	10 - 25	5.0 - 5.5
	Sandy	<10	2 - 10	<5.5
Sensitive	Clayey	>35	25 - 40	4.5 - 5.0
	Loamy	10 - 35	10 - 25	5.0 - 5.5
	Sandy	<10	2 - 10	<5.5

(After Wang and Coote, 1981)

TABLE 2 SENSITIVITY OF SOILS TO ACID PRECIPITATION

- 1 Nonsensitive areas (NS)
 - (a) all soils with free carbonate in the top 25cm
 - (b) all soils subject to frequent flooding
 - (c) all soils with an average CEC >15.4 meq per 100g in the top 25cm.
- 2 Slightly sensitive areas (SS) areas not included in 1a or 1b, that have an average CEC, in the top 25cm, of 15.4 - 6.2 meq per 100g.
- 3 Sensitive areas areas not included in 1a or 1b that have an average CEC, in the top 25cm, of < 6.2 meq per 100g.

(After McFee 1980)

TABLE 3 CATEGORIES ADOPTED FOR CLASSIFICATION OF THE SOLID GEOLOGY MAP (1:625,000) OF THE UK, ACCORDING TO SENSITIVITY TO ACIDIFICATION.

Category	Buffer capacity and/or impact on groundwaters	Rock type
1	Most areas susceptible to acidification, little or no buffer capacity, except where significant glacial drift.	Granite and acid igneous rock, most metasediments, grits, quartz sandstones and decalcified sandstones, some Quaternary sands/drift.
2	Many areas could be susceptible to acidification. Some buffer capacity due to traces of carbonate and mineral veining.	Intermediate igneous rocks, metasediments free of carbonates, impure sandstones and shales, coal measures.
3	Little general likelihood of acid susceptibility except very locally.	Basic and ultrabasic igneous rocks, calcareous sandstones, most drift and beach deposits, mudstones and marlstones.
4	No likelihood of susceptibility. Infinite buffering capacity.	Limestones, chalk, domomitic limestones and sediments.

(From Kinniburgh and Edmunds 1984)

BIOLOGICAL DATA BASES

A Gee

When the Regional Water Authorities were established in 1974 a Water Archive System was developed under the direction of DOE to provide a common computer system for handling technical water data. Initially, it was envisaged that storage and retrieval facilities would be developed for features (river water quality sampling points, treatment works, gauging stations etc.) and for time-series water quality, quantity and biological data. Whereas comprehensive water quality and quantity systems were produced and have been operational for several years, little effective progress has been made in developing a biological archive.

Of the 5 Water Authorities which participated in the development of the Water Archive, only NWWA undertook to set up a biological system. To be effective a biological archive has to be highly flexible in order to accommodate the widely differing requirements of biologists with respect to survey purpose, methodology and taxonomic penetration. A biological data-base should allow storage and selective retrieval of data obtained from algal, macrophyte and invertebrate sampling etc. These include site descriptions as well as qualitative and quantitative information on occurrence of different organisms. Unfortunately, the system which NWWA tried to devise proved too complex and work on the biological archive was abandoned.

Given the large amount of computer support required to produce and maintain a true biological archive using COBOL and FORTRAN programmes, it is unlikely that further progress will be made until data-base systems such as ORACLE are established and widely available. Data-base systems for biological information are currently being set up by a number of organisations eg. the US EPA ERAPT system and the University of Nottingham's Rural Wales Terrestrial Database (WALTER).

In the meantime, biologists in the water industry, FBA and elsewhere have developed their own methods of storing and manipulating biological data on mainframes and PCs. These alternative systems are, however, less flexible than the Water Archive proposals and do not easily allow statistical manipulation with data from the quality and quantity archives. In order to be widely used, common coding systems are clearly necessary. Although a Biological Determinand Dictionary Working Group produced a coding system which allowed for different levels of taxonomic penetration, this has not been universally adopted.

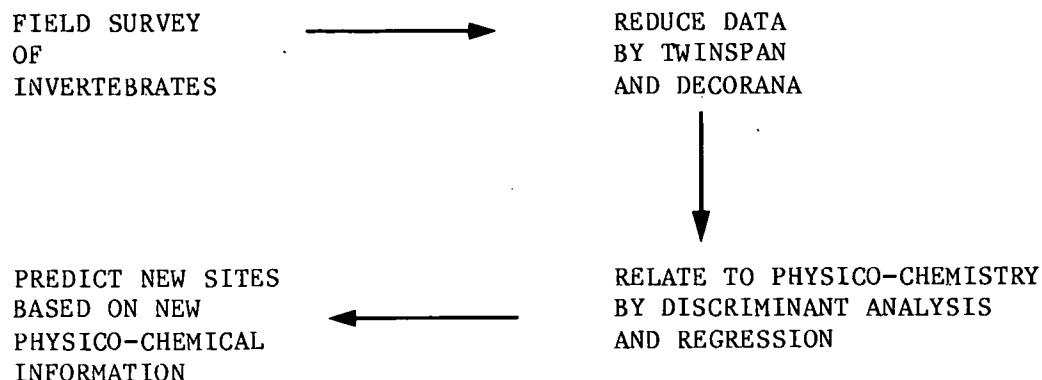
Although the present biological archive systems are less than ideal, they do, nevertheless, permit a high degree of data manipulation. For example, in Welsh Water the following programmes and their associated macros are available:

<u>PROGRAM</u>	<u>MACRO</u>	<u>DESCRIPTION</u>
BI00	VALIDATE	Validates features of matrix and reformats
BI01	SELECT	Extracts species data for plotting by BI02
BI02	PLOT	Produces plot file from output of BI01
BI03	PROCESS	Matrix conversion, masking program
BI04	ANALYSE	Calculates indices and coefficients for dendogram
BI05	DEND	Run For ANALYSE to produce Dendogram
BI06	SUMMARY	Summarises species presence for all biomatrices
BI07	SEARCH	Locates species occurrence in user's BIOMATRIX
BI08	NODEL	Produces large dendogram form BI04 output

<u>PROGRAM</u>	<u>MACRO</u>	<u>DESCRIPTION</u>
BI09	MERGE	Merges matrices to form single matrix
BI10	FORMAT	Extracts data from DOE 1980 survey
BI11	SWAP	Transfers Grid references from DOE file
BI12	CONVERT	Amalgamates species totals & log abundance, presence/absence
BI13	INDEX	Produce index of matrices in Biomatrix
TWINSpan	TWINSpan	Twinspan analysis of file produced by BI03
DECORANA	DECORANA	Decorana " " " " " "

These routines are used to manipulate data held by each group of biologists in files called BIOMATRIX.

The current data source and manipulation facilities can be used to model biological systems from physico-chemical data. For example, the following procedure has been applied to acid waters data:



The principal drawback of the present system is that each operation has to be carried out on highly specific data-sets, eg there is little flexibility in a file set up specifically for TWINSpan or DECORANA. Subsequent data manipulation also involves processes which are specific to the analysis required.

Until a comprehensive biological data-base system is established, it is likely that biologists will continue to work in isolation and much potentially useful biological information will be unavailable except to those who generated the data.

CHEMICAL DATA BASES

B Reynolds, R Harriman and M Hornung

SUMMARY

Five main purposes for collecting hydrochemical data and establishing data bases have been identified. These include:

- i) the assessment of long term trends in water quality;
- ii) process studies within catchments;
- iii) modelling studies;
- iv) the assessment of the effects of changes in the chemical composition of water on biological processes in streams and lakes;
- v) regional surveys of surface water quality.

Each of these aims has very different data requirements. Sampling strategy, catchment size and the careful selection of chemical parameters can be identified as key factors in obtaining useful and reliable data. Additional information from different sources may also be required and this can include hydrological data, rainfall chemistry data, geological and soils information. Of great importance is the quality of the chemical data. Techniques appropriate to low conductivity acidic waters must be used and validated with regular analytical quality control (AQC) checks on all parameters. The determination of pH and alkalinity are seen to present particular analytical problems. Available chemical data bases are assessed in relation to the requirements of the aims listed above, and areas where little or no data exist identified. Of equal importance, though generally more difficult to determine, is the quality and inter-comparability of chemical data, particularly where records extend back over a number of years.

INTRODUCTION

A large variety of chemical data bases relating to surface water quality have been compiled by bodies as diverse as university departments, research organisations (both commercial and government funded) and the various parts of the water industry. The data cover a wide range of determinands, large geographical areas and, in some cases, long periods of time. In order to focus on information relevant to the problem of surface water acidification, these data have to be sorted in some way. The key question to be asked of a data set in order to do this is simply, "why is the data set being collected?" In answer, five main purposes for data collection can be identified and these are:

- 1) the assessment of long term trends in water quality;
- 2) regional surveys of surface water quality;
- 3) process studies within catchments;
- 4) modelling studies;
- 5) the assessment of the impact of changes in water chemistry on the biology of streams and lakes.

Each of these aims has very different data requirements, and factors to be considered include: sampling frequency, parameters to be measured, data quality, location and scale of study (ie stream order or lake size) and length and continuity of records over time.

This paper intends to discuss the five purposes for data collection in two

ways. Firstly, in "conceptual" terms by examining the factors listed above and secondly by looking at the availability of appropriate data bases in order to identify areas with little or no information.

QUALITY OF CHEMICAL DATA

The quality of chemical data is fundamental to any discussion of chemical data bases. There are a variety of different problems associated with each relevant chemical determination, but it is beyond the scope of this paper to discuss each of these in detail. However, some general points will be made here concerning data quality relevant to the five purposes for data collection outlined above.

The quality of chemical data over time and comparability between data sets from different laboratories is often uncertain. There are a number of reasons for this. Changes in analytical technique, usually accompanying improvements to methods or equipment, can introduce large systematic errors. Undetected operator errors, equipment malfunction and the use of an inappropriate method will also introduce bias. This can apply not only to the analysis itself, but also to sampling, sample storage and handling and any pre-treatment such as filtering. The purpose for which the measurement is being made will determine the accuracy of the result. This has a particular bearing on historical data where acidification may not have been the original reason for starting a monitoring study for which lower levels of accuracy were acceptable. These problems are compounded when data sets from different organisations are compared where differences in techniques and equipment introduce another dimension of error. The results of inter-laboratory comparisons demonstrate this point well (Gardner, 1985).

Of all the measurements relevant to the study of low conductivity acidic waters, the determination of pH is perhaps the most prone to error. Under favourable conditions, the total error on a single result can be less than ± 0.2 pH units (Gardner 1985). Much larger errors ± 0.5 pH units can easily arise, however. The use of inappropriate equipment, variations in responses between electrodes and non-theoretical behaviour of electrodes can all be responsible for this (Illingworth, 1981; Covington et al, 1983; Neal & Thomas, 1985). Given the weight often placed on pH results in studies of acid waters, it is vital that precise details of equipment and methods are known so that available data sets can be interpreted realistically. Future studies should attempt to standardise on sound methods and equipment. Regular inter-laboratory analytical quality control (AQC) exercises should also be conducted to assure data quality.

Alkalinity determinations often accompany pH measurements. This analysis is also particularly prone to error, largely due to a failure to appreciate the meaning of the concept and its application to acid waters. Titration to a fixed endpoint pH is commonly used to determine alkalinity, but it has been shown that this is completely inappropriate for acid waters (Skeffington, 1985a) and may introduce very large errors. Again future studies should endeavour to standardise on appropriate methods (eg Gran titration) and encourage regular AQC exercises both within and between laboratories.

PURPOSES FOR DATA COLLECTION

- 1) Assessment of long term trends

This aim is perhaps the most easily satisfied in terms of sampling and analytical requirements. Regular spot samples or weekly composite samples at a fixed site will provide the basic information, and only a restricted number of key parameters need to be determined. Streamflow, pH, acidity,

alkalinity and calcium concentration would be an adequate minimum for a meaningful data base (UKAWRG, 1986).

The scale of the study and sampling location are particularly important, as waters which may be vulnerable to acidification are restricted to headwater streams and lakes. Sampling low down the river system yield data for which any evidence of acidification is confounded by other factors. These include the influence of an increased proportion of groundwater containing acid buffering ions entering the system, plus the effects of runoff from intensively managed lowland agriculture. Inputs of industrial effluents and wastewater will also affect stream chemistry in the more populated lowland areas. The choice of sites should encompass a broad spectrum of headwater catchments ranging from those which might be classified as "sensitive" to acidification to those which could be termed "insensitive". The nature of the atmospheric inputs should also be considered so that polluted areas as well as "pristine" locations are included. Some form of catchment classification, using information such as bedrock geology, soil type, land-use and vegetation, together with data on atmospheric inputs, would be a necessary step in selecting monitoring sites. Small lakes are probably better monitoring sites than streams as lakes are less sensitive to the effects of hydrological changes, although large lakes would be unsuitable due to long turnover times. Conversely, small first order streams exhibit extreme responses to changes in hydrological conditions and are very sensitive to local variations in geology, soil type and land use (Hornung et al, 1985; Neal et al, in press). Thus, the choice of catchment for a long term monitoring exercise reflects a balance between an appropriate location in a headwater area, a reasonably "damped" hydrological behaviour and a representative integration of the effects of land use, soil type and geology.

The length and continuity of records and data quality are vital factors in long term trend analysis. Ideally, the requirement is for samples taken at regular intervals over an extended period of time; an apparently simple task. However, as discussed earlier, it is difficult to ensure the quality of chemical data over time and comparability between data sets from different laboratories.

The UK Acid Waters Review Group (UKAWRG) has recently completed an analysis of long term chemical data bases (UKAWRG, 1986). One hundred data sets were obtained extending over a ten year period (1974-1984) from a variety of organisations. Statistical analyses of trends in pH were attempted, but these were seriously hampered by the lack of uniformity in the data sets. Irregular sampling frequency and long gaps in the records mostly contributed to this. The UKAWRG were forced to conclude that the data they examined left much to be desired in terms of the location of monitoring sites and the frequency and regularity of sampling. In addition, much data collected routinely by the water industry and for the Harmonised Monitoring Scheme (Brown et al, 1982) had to be omitted, as sample sites were too low down the river system to provide information indicative of possible acidification trends.

2) Regional surveys of water quality

The requirements for regional surveys of water quality are similar to those for studies of long term trends, except for the fundamental difference in sampling strategy. The aim is to sample across a wide geographical area in a short time period so that the effects of streamflow on water chemistry are minimised. This is best achieved by sampling at baseflow. These data will reveal the influence of bedrock geology on water chemistry (eg Walling & Webb, 1981; Adamson & Benefield, in press), but yield little information on

the effects of land use. The latter become more apparent if stormflow data are either included in the analysis of the total data set (eg Osborne et al, 1980) or are examined separately (eg Neal et al, in press). Thus, more may be learned from a programme of regular sampling across all the sites or by sampling at baseflow and at selected periods of high flow. These approaches will be more demanding on resources, however, but would be amenable to collaborative work by a number of organisations.

The location of sampling sites is important if the results are to be applied in an acidification context. Again, headwater or low stream order sites should be selected to include a representative number catchments covering the range of likely susceptibilities to acidification and any variations in atmospheric inputs across the area. A classification exercise may be required to reduce the survey sites to a manageable number. However, even within areas identified as having acid waters, local variations in geology, soils and land use, not apparent from map data, may have an overriding effect on streamwater chemistry (UKAWRG, 1986; Reynolds et al, in press).

Regional surveys of water quality are a valuable tool for highlighting areas for further study. So far there has been no co-ordinated approach to survey work, although data sets have been collected for a number of areas by different organisations. These include surveys of lochs and streams by various River Purification Boards and the Freshwater Fisheries Laboratory in Scotland, a survey of Derbyshire Peak District streams and Welsh lakes by CERL (Brown & Martin, 1980 and Sadler et al, 1982 respectively) and a year long survey of streams in Wales by Welsh Water Authority. An assessment of the susceptibility of UK groundwaters to acid deposition has also been completed by the British Geological survey (Kinniburgh & Edmunds, 1984) and other survey work is also being undertaken. A collective examination of this body of data would, therefore, provide a valuable baseline for future acidification studies and be a precursor to future co-ordinated regional surveys.

3) Process studies

Process studies are designed to elucidate the mechanisms operating within a catchment. The sampling strategy should aim to cover the events which yield the most information about the system. Thus sampling interval will vary according to weather conditions. Infrequent sampling may be sufficient to characterize baseflow chemistry, whereas automatic equipment sampling at 0.5hr to 2hr intervals or continuous monitoring would be required to follow storm events. A variety of events need to be studied to cover the range of stream chemical responses and antecedent conditions and will include acid rain episodes, rain after long dry periods, clean rain episodes, sea-salt episodes, snow-melt etc. Routine monitoring can also be undertaken to provide information on seasonal trends in stream chemistry as often demonstrated, for example, by NO_3 (Roberts et al, 1984). Much may be learned from a single year study with very intensive effort, but a longer experiment (c.3 years) is preferable to account for the effects of any anomalous climatic conditions.

A wide range of chemical determinands are required for process studies including major cations and anions, trace metals, TOC Si, F, Al, organic acids etc. Attention must be paid to the quality of the chemical data. Other "accessory" parameters are also needed such as the chemistry of atmospheric inputs, throughfall beneath the vegetation and soil waters, meteorological and hydrological data together with details of geology, soils and vegetation cover.

Choice of site is important. Catchments of first or second order streams

are the most appropriate. These are hydrologically responsive and can be selected so that they are geologically uniform with a restricted range of soil and vegetation types.

Catchment based process studies can be supplemented in two ways. Firstly, field or laboratory experiments can be undertaken to gain a detailed understanding of relevant processes occurring, for example, in the soils of the catchment using plot scale or soil column experiments. Alternatively, a series of small catchments with similar geology and soils but under different land uses can be selected so that the impact of land use on stream water chemistry can be assessed. This approach can be further extended by choosing a series of sites which hold other factors constant. Again, a range of catchments from "strongly acidified" through to "pristine" should be studied, together with sites in different atmospheric pollution environments. Clearly, this scale of project is beyond the scope of any single research organisation, and points to the value of funding co-ordinated research programmes such as SWAP (Mason & Seip, 1985).

There is a growing body of literature on catchment based process studies in the UK. However, much of this has been presented from a geomorphological, geochemical or ecological perspective with little direct reference to acidification (eg Cryer, 1976; Waylen, 1979; Reid et al, 1981 (a&b); Foster & Grieve, 1984). Other work has been concerned with catchments where acidification is unlikely to be a problem (eg Edwards, 1973; Foster, 1979). More recently, a large number of studies relevant to acid waters have commenced, reflecting an increasing awareness of the problem and initiatives for funding research, eg the SWAP project. Unfortunately, there is no formal register of all the relevant projects, although a list has been compiled informally by the workshop (Appendix 2). Much of the work is current and therefore results are as yet, largely unpublished however, some information is available (see eg Skeffington, 1985b) and clearly more can be expected.

4) Modelling studies

The subject of catchment modelling will be covered by another paper at this meeting. Consequently, the topic will only receive brief treatment here.

Modelling studies are often linked to, or form an integral part of, process studies and utilise the data obtained from them. Many of the models of catchment processes/stream chemistry currently available require an intensive input of one or more parameters. These usually include a stream chemical term (eg pH) together with detailed hydrological and meteorological data, plus rainfall chemical parameters depending on the sophistication and objectives of the model (see eg Johnson et al, 1969; Christophersen et al, 1982; Booty & Kramer, 1984, Cosby et al, 1985). Other factors, such as aspects of the geography of the catchment (eg slope and percent vegetation cover) and the physical, chemical and hydrological properties of the soils (eg porosity and cation exchange capacity) may also be needed. Sampling interval is of key importance, as frequent samples (2-3 times per week) or continuous monitoring are often required. If input-output budgets are to be estimated then frequent sampling is needed to validate streamflow/chemistry relationships. Flow proportional composite samples can be used to avoid the uncertainties of solute rating curve analysis. Chemical inputs from the atmosphere are also necessary along with water balance information. The length of study will be significant for mass-balance calculations, as anomalies in climate may dramatically affect solute budgets over a short (1 year) time period.

Another aspect of modelling is the use of thermodynamic chemical equilibrium

models such as WATEQ (Truesdell & Jones, 1974), WATSPEC (Wigley, 1977) or GEOCHEM (Sposito & Mattigod, 1980). These provide a useful means of examining the equilibrium chemistry and speciation of elements such as Al and heavy metals associated with catchment acidification. The models require high quality chemical data for a wide range of determinands together with variables such as water temperature and Redox potential. However, they should be used carefully with an appreciation of their limitations and the assumptions they contain. For example, equilibrium conditions are assumed and the reliability of some of the thermodynamic data may be uncertain. Where conflicting thermodynamic data exist, the choice of data can greatly influence the predictions of the model (eg French, 1985).

Many of the studies referred to in Appendix 1 incorporate data acquisition techniques applicable to, or specifically designed for, modelling purposes. For example, the Esk-Duddon study and the Llyn Brianne study, amongst others, employ continuous monitoring for a number of water quality, hydrological and meteorological parameters. Other studies which now have long data runs, though with less frequent sampling (eg Plynlimon), could also be interrogated profitably by appropriate models.

5) Assessment of stream chemistry effects on aquatic biota

The assessment of the effects of surface water acidification, and associated factors, on stream biota bring together the topics already discussed and draw on the information they supply. For field observational studies, directly concerned with effects on aquatic biota, key chemical parameters, such as pH, Ca, Na and Al can be identified and measured. In particular, the chemical speciation of Al is important for fisheries studies (Driscoll et al, 1980).

To observe short term biological responses to stream chemistry in the field, sampling should concentrate on episodes, so that "worst" situations are identified. Spot or automatic sampling can be used and low flow sampling is not required. However, the short term response maybe superimposed on a long term trend, and appropriate sampling and chemical analysis will be needed to determine this.

Observational work can be supplemented by field experimental studies. This may involve the addition of biological material into the stream (eg. fish eggs) and observing its response to natural variations in stream chemistry. Alternatively, the stream or catchment can be manipulated, (eg. by liming or acid addition) and the effects observed either on the naturally occurring biota or on material added experimentally. For all these approaches, experimental design will determine site, sampling and analytical requirements. Complementary laboratory studies and bioassay together with physiological studies can also be undertaken.

Fisheries problems have been responsible for initiating many of the UK studies of acidified catchments, (eg Harriman & Morrison, 1982; Stoner et al, 1984). A large amount of relevant international literature exists describing both field and laboratory studies linking surface water acidification to fisheries problems, and this has been reviewed in detail quite recently (Howells, 1983). The conclusions of this review point, however, to serious gaps in our understanding of the relationships between acid surface water and fisheries problems. For example, the extent and duration of acid episodes is largely unknown and it is not clear whether reported fishery decline reflects the effects of accrued damage due to these episodes or the effects of prolonged adverse water quality. Some of the studies already mentioned in Appendix 1 will help answer these questions, but there is much to be gained from catchment process studies which

integrate with biological work at the same site, eg the Loch Fleet and Llyn Brianne studies.

CONCLUSIONS

Several points emerge from this discussion of chemical data bases in relation to catchment acidification.

- 1) The quality of "historical" chemical data is generally poor. In many cases, the data were collected for other purposes and insufficient attention was given to maintaining a programme of regular sampling. Additionally, inappropriate analytical methods for key parameters, for example pH, have often been employed in the past.
- 2) Future work must carefully consider the use of appropriate analytical methods, particularly for pH and alkalinity. Regular inter-laboratory AQC exercises, such as those run by the Water Research Centre and Forth River Purification Board, should be undertaken to check and improve upon techniques of sampling, sample handling and storage, and analysis of natural waters.
- 3) There is a need for a co-ordinated approach to the assessment of long term trends and regional surveys of water quality. The UKAWRG has made a start on this; perhaps a "Harmonised Monitoring Scheme" for catchments susceptible to acidification is required? A collective examination of available regional survey data is a necessary first step.
- 4) A large number of complex processes determine the effects of acid deposition on catchment stream water quality. Thus, there is a continuing need for a multi-disciplinary approach to catchment studies, incorporating predictive modelling. Topics such as the interaction of atmospheric deposition with the vegetation canopy, detailed hydrology, soil chemical processes, speciation of aluminium and quantification of weathering rates should form a part of these studies. The chemistry of potentially toxic heavy metals (eg Cd and Mn), the effects of biological activity (eg respiration) on stream acidity, the kinetics of important reactions (eg Al-organic complex formation) and the role of naturally occurring organic acids should also be examined.
- 5) The rates of natural acidification processes within catchments need to be quantified so that the effects of acid deposition can be placed in context. To complement this, the impact of land-use change on both natural and "man-induced" catchment acidification should also be assessed.

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MODELLING STREAM ACIDITY IN UK CATCHMENTS

P G Whitehead & C Neal

SUMMARY

As part of the joint British-Scandinavian Surface Waters Acidification Programme, the Institute of Hydrology is establishing catchment studies in Scotland and Wales. Data from these catchment studies are being used to develop a range of models for investigating short term and long term changes in catchment acidity. Information on the modelling techniques available at IH is presented together with applications of the models to catchments in Scotland and Wales.

INTRODUCTION

Catchment studies investigating the acidic behaviour of upland streams are expensive, time consuming and difficult to establish due to the complexity of hydrological, chemical and biological interactions. Nevertheless many catchment studies have been and are being established to evaluate short term and long term fluctuations in stream water chemistry. For example, as part of the joint Scandinavian - British Surface Water Acidification Programme (SWAP), (Mason & Seip, 1985) major studies are being established in the UK and Scandinavia. Other organisations such as the Welsh Water Authority (Llyn Brianne Study; Stoner *et al*, 1984) the Solway River Purification Board (Loch Dee study; Burns *et al*, 1982) and the Freshwater Fisheries Laboratory (Loch Ard Study; Harriman *et al* 1981) have also established catchment studies following mounting concern over the loss of fisheries in Scotland and Wales and the possible detrimental effects of stream acidity on water resources. Several researchers involved in these studies (Harriman *et al*, 1981; Gee & Stoner, 1984) have reported elevated acidity and aluminium levels in upland streams draining afforested (conifer) catchments in the UK. Moreover in many of these areas and particularly forested catchments, fisheries have deteriorated and restocking programmes have been unsuccessful.

It is with these problems in mind that IH has established a catchment study in Wales at Plynlimon (see Neal *et al*, 1985). IH is also establishing a catchment study in the Cairngorm region of Scotland in collaboration with DAFS (Department of Agriculture and Fisheries for Scotland), the Macaulay Institute of Soil Science and Imperial College, Department of Civil Engineering. IH is responsible for providing stream gauging, rainfall stations, a weather station, snow surveys, sampling and continuous water quality monitoring. IH is also responsible for the subsequent data management, analysis and interpretation. DAFS is responsible for all chemical and biological analysis, with the exception of snowmelt chemistry, which would be undertaken by IH. The Macaulay Institute is responsible for soil-surveys and soil-water chemistry and Imperial College are establishing plot studies.

The hydrological and chemical data collected from the catchment studies forms the basis of a comprehensive modelling research programme by IH.

Recently there has been considerable use of mathematical models to describe the dominant interactions and processes operating in catchments and to simulate catchment behaviour. Steady state models have been used prescriptively to demonstrate the long term consequences of changes in the industrial emissions of SO_x (Cosby *et al*, 1985 b; Kamari *et al*, 1984). Correspondingly, dynamic models have been successfully applied descriptively to several catchments (Christopherson *et al*, 1982, 1984). For example,

Christophersen et al. have developed a simple conceptual model that reproduces major trends in chemical and hydrological behaviour in Norwegian catchments. This model has been successfully extended (Seip et al., 1985) and applied descriptively to the Harp lake catchment in Canada. The model has also been applied to two forested catchments in Sweden (Grip et al., 1985).

A wide range of mathematical modelling techniques are available at IH for analysing catchment data. These include CAPTAIN (Computer Aided Package for Time Series Analysis and the Identification of Noisy Systems; Venn and Day, 1977; Whitehead et al., 1986a), MIV (Multivariable time series model, Young and Whitehead, 1977), the BIRKENES model (Christophersen et al., 1982), MAGIC (Cosby et al., 1985), EKF (Extended Kalman Filter, Beck and Young, 1976) TOPMODEL (Beven, 1982) and IHDM (Institute of Hydrology Distributed Model, Morris, 1980).

In this paper several of these techniques are described and applied to investigate short term catchment responses or 'events' and long term acidity of soil and stream waters.

TIME SERIES OR 'EVENT' TYPE MODELS AND THEIR APPLICATION TO LOCH DEE

Time series models are suitable where the overall input-output behaviour is of prime importance and where internal mechanisms are particularly complex. It is assumed that a 'law of large systems' applies (Young, 1978) whereby the combination of all the complex non-linear and distributed elements gives rise to an aggregated system behaviour that is relatively simple in dynamic terms.

Loch Dee has a remote setting in the Galloway Hills in South West Scotland. The catchment is made up of 3 sub-basins: Dargall Lane to the west, White Laggan Burn with its tributary the Black Laggan towards the south, and Green Burn entering from the south east. The outflow at the north east end of the loch is the source of the River Dee and up to this itself occupies 1.0 km. Catchment altitudes range from 225 m on the Loch shore to 716 m on Lamachan at the head of the Dargall Lane. Nearly two thirds of the catchment lies above 305 m (1000 ft). Geologically the area comprises two distinct rock types: Ordovician greywackes/shales and granites of Old Red Sandstone Age (Burns et al., 1982).

In Loch Dee an extensive record of hydrological water quality data has been collected over a five year period (Burns et al., 1982; Langan, 1985). Analysis has been restricted initially to a time series model relating flow to hydrogen ion concentration for the white Laggan sub-catchment. The White Laggan is subject to episodic acidification, primarily attributed to atmospheric inputs (Langan, 1985).

The model fitted is an autoregressive moving average type of the form

$$x_t = -\delta_1 x_{t-1} + \omega_0 u_t$$

where X_t is the hydrogen ion concentration ($\mu\text{eq l}^{-1}$) and u_t is the flow ($\text{m}^3 \text{sec}^{-1}$) in the stream at time t .

The parameters δ and ω were estimated using a time series algorithm applied to 200 hourly observations of pH and flow. The parameters were estimated to be;

$$\delta_1 = -0.680 \text{ (standard error 0.012)}$$

$$\omega_1 = 0.659 \text{ (standard error 0.022)}$$

and Figure 1 shows the simulated hydrogen concentration against the observed

concentration. A remarkably good fit to the data is obtained with 93 of the variance explained and suggests that H ion and flow are closely related. However a true test of the model would be to use an additional data set; Langan (pers comm) has applied the approach to all three subcatchments of Loch Dee and found that equally good models have been obtained for a wide range of storm events. In the case of the White Laggan a mean response time (T) of 2.6 hours is obtained, reflecting the fast response time between output flow and hydrogen ion concentrations.

Further applications of the time series techniques to data from Welsh and Norwegian catchments are given by Whitehead et al (1986).

APPLICATIONS OF THE 'BIRKENES' MODELS

A second class of models have been applied to data from the Loch Dee study. These include the 'Birkenes' model developed by Christophersen et al (1982, 1984).

The model comprises of a simple two-reservoir hydrological model operating on a daily timestep upon which has been superimposed the important chemical processes that control the acidification of catchments. Inputs to the model are precipitation, mean daily temperature, mean daily soil temperature and sulphate deposition rates. Figure 2 shows the principal hydrological and chemical processes operating.

The model outputs daily concentrations of hydrogen ion, aluminium sulphate, calcium + magnesium (M^{2+}) and bicarbonate in the stream along with predicted flow.

Numerous modifications and additions over the years have resulted in the program structure becoming somewhat confused. Therefore the model has been extensively re-written at IH so as to greatly increase computational efficiency and improve the readability of the FORTRAN 77 source code and hence simplify the task of making modifications in the future.

The 'Birkenes' model has also been used to assess the sensitivity of stream acidity to hydrological parameters and changes in baseflow.

Flow movement between the soil and groundwater compartments is restricted by a "percolation" equation as follows:

$$A_{SIG} = P - (B - B_{min})/B_{max} \quad \text{for } B > B_{min}$$

$$\text{and } A_{SIG} = 1.33P - 0.33P(B/B_{min})^3 \quad \text{for } B < B_{min}$$

where B refers to the groundwater compartment water level and B_{min} and B_{max} refer to minimum and maximum water levels respectively (see Figure 2). The parameter, P, can be considered as a percolation parameter so that increasing P increases the fraction of flow, A_{SIG} , routed to the lower reservoir. This leads to an increase in the baseflow contribution to the stream. The model also includes a piston flow component to describe the hydraulic movement of water out of the groundwater compartment.

The changes in stream water concentrations for H^+ ion and Al^{3+} to changes in the baseflow contribution to streamwater is highly non linear. This is illustrated in Figures 3 and 4 which show H^+ and Al^{3+} maximums and means over a range of baseflow conditions for both the long and short term data sets: all concentration values fall as the baseflow increases, the rate of decrease varying from one variable to another. In general, increase in baseflow results in significant reductions in H^+ ion and Al concentrations.

Studies by Seip and Rustad (1983) show a similar non linear behaviour when upper and lower soil horizon waters are mixed.

Further results are given by Whitehead et al (1986b) and confirm the sensitivity of the model to parameter, and hence baseflow, changes.

APPLICATION OF MAGIC TO LOCH DEE

MAGIC (Model of Acidification of Groundwater In Catchments; Cosby et al, 1986a) is explicitly designed to perform long term simulations of change in soilwater and streamwater chemistry in response to changes in acidic deposition. The processes on which the model is based are:

- anion retention by catchment soils (eg sulphate adsorption);
- adsorption and exchange of base cations and aluminium by soils;
- alkalinity generation by dissociation of carbonic acid (at high CO₂ partial pressures in the soil) with subsequent exchange of hydrogen ions for base cations;
- weathering of minerals in the soil to provide a source of base cations;
- control of Al³⁺ concentrations by an assumed equilibrium with a solid phase of Al(OH) .

A sequence of atmospheric deposition and mineral weathering is assumed for MAGIC. Current deposition levels of base cations, sulphate, nitrate and chloride are needed along with some estimate of how these levels had varied historically. Historical deposition variations may be scaled to emissions records or may be taken from other modelling studies of atmospheric transport into a region. Weathering estimates for base cations are extremely difficult to obtain. Nonetheless, it is the weathering process that controls the long term response and recovery of catchments to acidic deposition, and some estimate is required.

The MAGIC program has been applied to the Dargall Lane sub-catchment in Loch Dee and a detailed description of the application is given by Cosby et al (1986b).

Several chemical, biological and hydrological processes control stream water chemistry. These processes are often interactive and not easily identifiable from field observation. Modelling allows separation of the different factors and the establishment of their relative importance quantitatively. Here the factors considered are afforestation, dry and occult deposition, variations in acidic oxide loading and deforestation.

LONG TERM ACIDIFICATION TRENDS FOR DARGELL LANE

Figure 5 shows a simulation of long term acidity for the Dargall Lane catchment. The sulphate deposition history is shown in Figure 5a and this 'drives' the MAGIC model. The historical simulation of pH shown in Figure 5b is similar to the values obtained from the diatom records of lochs in the region in that a significant decrease in pH from 1900 onwards is inferred. The steeper decline from 1950 to 1970 follows from the increased emission levels during this period. The model can also be used to predict future stream water acidity given different future deposition levels. For Dargall Lane, stream acidity trends are investigated assuming two scenarios for future deposition. First, assuming deposition rates are maintained in the future at 1984 levels, the model indicates that annual average stream pH is likely to continue to decline below presently measured values. Second, assuming deposition rates are reduced by 50 from 1984 levels (between 1985 and 2000) the results indicate that current stream water acidity will be

maintained (Figure 5b). Further details of the application of this model are given elsewhere. Note an increase in stream water pH about 1980; this follows a significant drop in sulphur emissions during the 1970s. Note also that an earlier decline in streamwater acidity is predicted if there had been no reductions in emissions since 1970.

AFFORESTATION

Afforested systems are more complex to model than grassland systems because the introduction of the forest perturbs a grassland ecosystem which in itself is difficult to model. The effects of the forest root system, leaf litter layer and drainage ditches will change the hydrological pathways; this will control the nature and extent of the chemical reactions in the soil and bedrock. Further, the additional filtering effect of the tree on the atmosphere will enhance occult/particle deposition and evapotranspiration will increase the concentration of dissolved components entering the stream. The magnitude of these different effects varies considerably; for example, evapotranspiration from forests in the British uplands is typically of the order of 30% of the precipitation which is almost twice the figure for grassland. This will have the consequence that the total anion concentrations within the stream and soil water increase by 14% following afforestation. The forest will also increase anion and cation loading due to the enhanced filtering effect of the trees on air and occult sources. (Several forest catchment studies have shown that chloride concentrations are higher in streamwaters than in the corresponding rainfall or grassland streams. Such a difference results from dry and occult deposition, assuming that chloride is derived from a maritime source and not from leaching from the catchment bedrock. Such increases are typically of the order of 30%). The filtering effects will apply both to marine and pollutant aerosol components. Altering the hydrological pathways can also have a major effect on stream water quality since the forest tends to increase surface runoff thereby flushing/displacing highly acidic water from the surface layers; the soil zone acts as a proton and aluminium source whilst the bedrock, if silicate or carbonate bearing, provides proton consumption by weathering reactions. To illustrate the effects of afforestation simply in terms of increased concentrations from both enhanced dry deposition and evapotranspiration, the MAGIC model has been applied to the Dargall Lane catchment assuming that a forest is developed over the next 40 years. It should also be noted that, here, no allowance has been made for the effects of cation and anion uptake by the trees during their development; the incorporation of base cations into the biomass would result in an enhanced acidification effect during this period.

Of critical importance is the relative and absolute contribution of marine and pollutant inputs from dry and occult deposition. Figure 6 shows the effects of increasing evapotranspiration from 16 to 30% over the forest growth period with varying levels of marine, pollutant and marine + pollutant inputs. Increasing either marine or pollutant components leads to enhanced stream water acidity, the greatest effects being observed when both components are present; the effect of simply increasing evapotranspiration from 16 to 30% has a similar effect but the changes are much smaller. The important features of these results are the enhanced and acidic oxide inputs from increased scavenging by the trees result in a marked reduction in pH levels and that there is an additive effect when both processes are combined. These reductions are much greater than the effect of evapotranspiration.

ATMOSPHERIC ACIDIC OXIDE INPUTS

An important factor in determining stream acidity in the upland UK is the

level of acidic oxide deposition; rates of deposition (non marine wet deposition and dry deposition) can vary from 0.5 to over $6\text{ g S m}^{-2}\text{ yr}^{-1}$ and from 0.1 to over $0.5\text{ g N m}^{-2}\text{ yr}^{-1}$. Figure 7 shows the effects of such variations for both moorland and forested catchments; the highest levels correspond to areas with high atmospheric acidic oxide rates (3 times the historic and 1984 deposition levels observed in the Southern Uplands of Scotland). With increasing atmospheric acidic oxide pollution, the decline in stream pH is accelerated, the changes occur much earlier, and the final pH of the stream water is lower.

DEFORESTATION

Whilst afforestation increases stream acidity, as shown both by the model predictions and field evidence, then deforestation will result in a reduction in stream water acidity. Figure 8 shows the effects of deforestation from the present time for a range of acidic input loadings. The result shows that while there is a short term improvement in stream acidity, the long term acidification trend is maintained. It is interesting to note that the recovery following deforestation at the intermediate deposition levels is greater than that at the higher levels. This is because base saturation has not been completely depleted, and the reduced deposition following deforestation can be buffered by the available cations. Under the higher deposition levels base saturation is reduced to very low levels making recovery much less significant. Note that afforestation following tree harvesting will negate the improvement in stream water acidity.

IMPLICATIONS

The modelling enables assessment of the relative effects of atmospheric acidic oxide pollution and conifer afforestation, as well as highlighting some of the topics that need further consideration. For example, the long term trends in stream water acidification for the grassland catchment suggest that for at least part of the upland UK, acidic oxide pollutant inputs are the dominant source of increased stream water acidity. The model predictions are similar to observations of stream acidity found in Southern Scandinavia and add weight to the conclusion that such pollutant inputs are also a major source of stream acidification in those countries as well. How important this acidification process is on a regional basis in the upland UK cannot be gauged immediately because many unresolved factors remain, as mentioned above. However, much of the British uplands have soils which are susceptible to acidic inputs; it is therefore reasonable to assume the results of this present modelling exercise are widely applicable. If the above results are representative of sensitive upland areas then reductions in present acidic emissions of the order of 50% are required to prevent further increase in stream acidity moorlands; afforested catchments require greater reductions. The study points to the need for further regional analysis of soil and stream water chemistry, as well as a better understanding of hydrogeochemical processes operating within catchments. Further, the study provides an example of the need to establish the extent of scavenging of aerosols onto plant surfaces, and more generally on the benefits of multidisciplinary catchment studies. Finally, the detrimental effect on stream water quality caused by conifer afforestation in uplands subject to acidic deposition is irrefutable. While there is uncertainty regarding the nature and the extent of the hydrogeochemical processes operative there is a need to change existing forestry practices which are of immediate pragmatic concern.

CONCLUSIONS

The model techniques applied at IH have proved to be particularly useful yielding information on the catchment responses, processes and possible future behaviour.

On the hydrological side, time series techniques, lumped and distributed hydrological models are available. In the case of chemical processes, time series techniques can be applied but the principal models available at IH are the BIRKENES and MAGIC models. Modifications such as the introduction of sea salt will be necessary in the case of the BIRKENES model before application to the Loch Dee and Plynlimon catchments is possible. Also it may be necessary to reassess the dominant equilibria used in the model; for example, is aluminium controlled by $Al(OH)$, $Al(OH)SO$ or by $Al(OH)_{1-x}S_xO_2$? We hope to develop a modified and combined BIRKENES and MAGIC chemistry model and couple this with the distributed models to provide an additional tool with which to investigate catchment behaviour.

ACKNOWLEDGEMENTS

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Figure 1

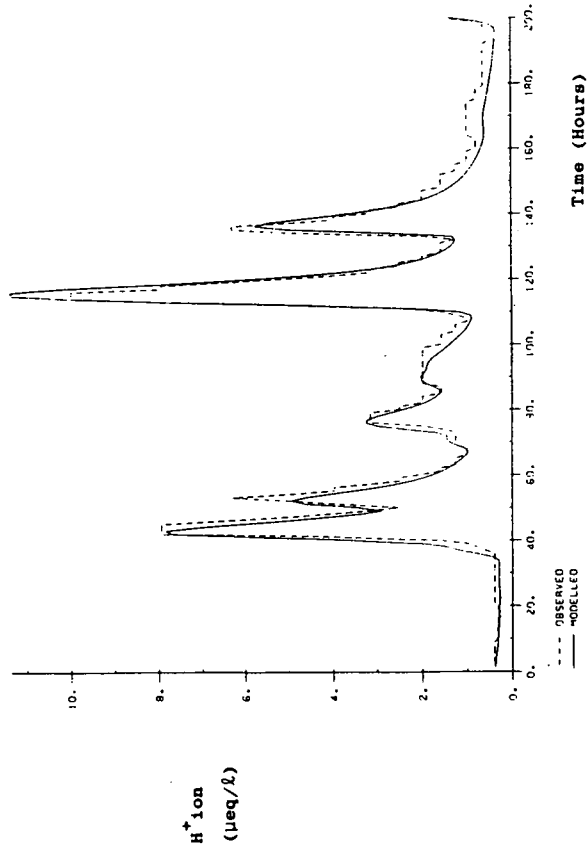
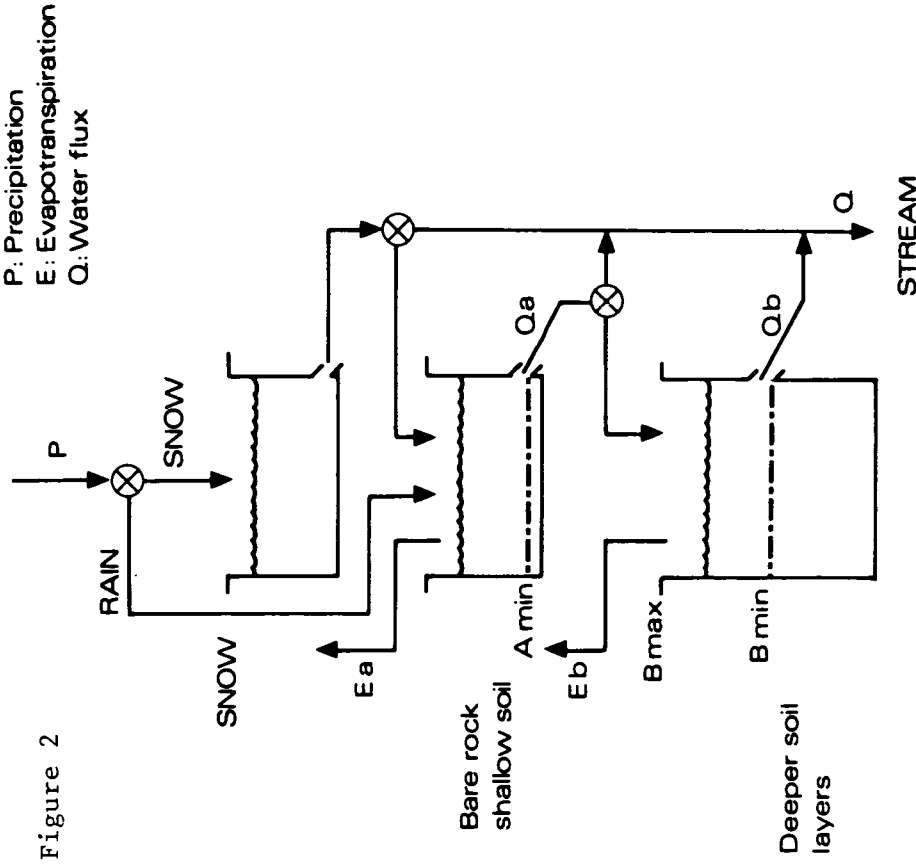


Figure 1 Simulated and Observed H^+ ion in the White Laggan, Loch Dee, Scotland, based on the Flow model.

Figure 2



STREAM

Figure 2 Hydrological Model used for Harp Lake Catchment and main processes operating.

	Shallow Soil Reservoir	Deeper Soil Reservoir
H_2O	Precipitation, evapotranspiration, infiltration to lower reservoir, discharge to stream	Infiltration, evapotranspiration, discharge to stream, piston flow
SO_4	Wet + dry deposition, adsorption/desorption, mineralization	Adsorption/desorption, reduction
$Ca + Mg$	Ion-exchange	Release by weathering, adsorption/desorption
H^+	Ion exchange and equilibrium with gibbsite	Consumption by weathering, adsorption/desorption, equilibrium with gibbsite
Al^{+3}	Equilibrium with gibbsite	Equilibrium with gibbsite, adsorption/desorption
HCO_3^-		Equilibrium with a seasonal varying CO_2 pressure

Figure 3 Maximum H^+ and Al^{3+} concentrations in the stream showing variation over a range of baseflow conditions (Three Year Simulation 1977-1980).

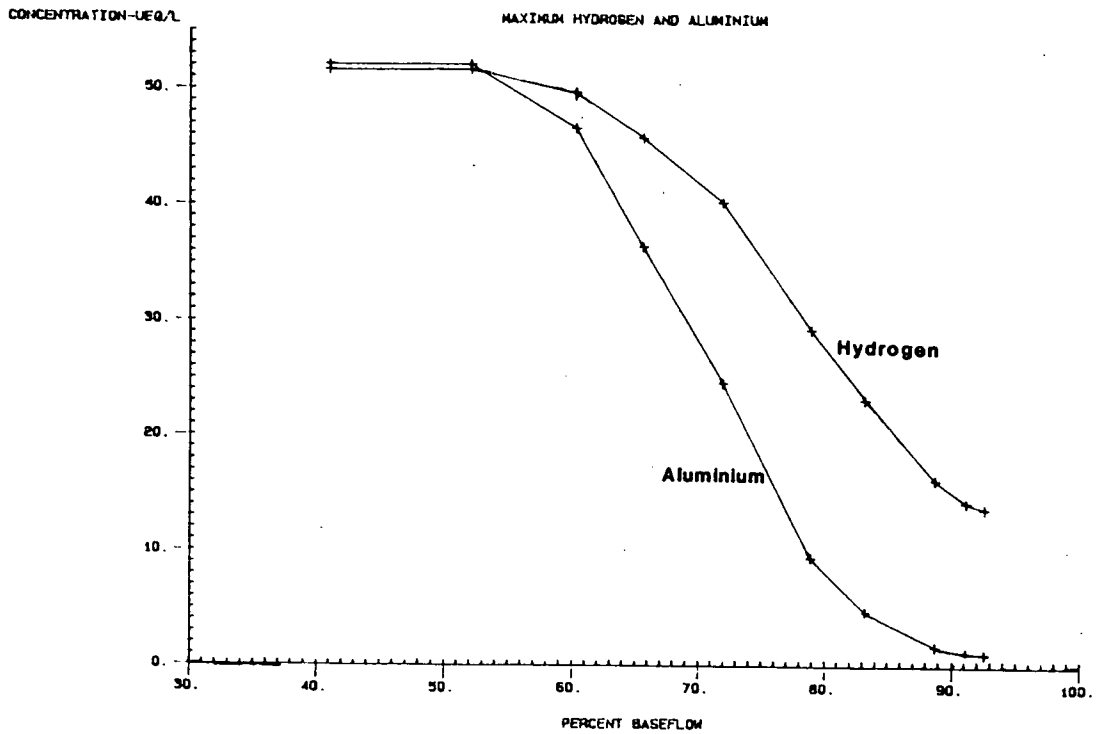


Figure 4 Mean H^+ and Al^{3+} concentrations in the stream showing variation over a range of baseflow conditions (Three Year Simulation 1977-1980).

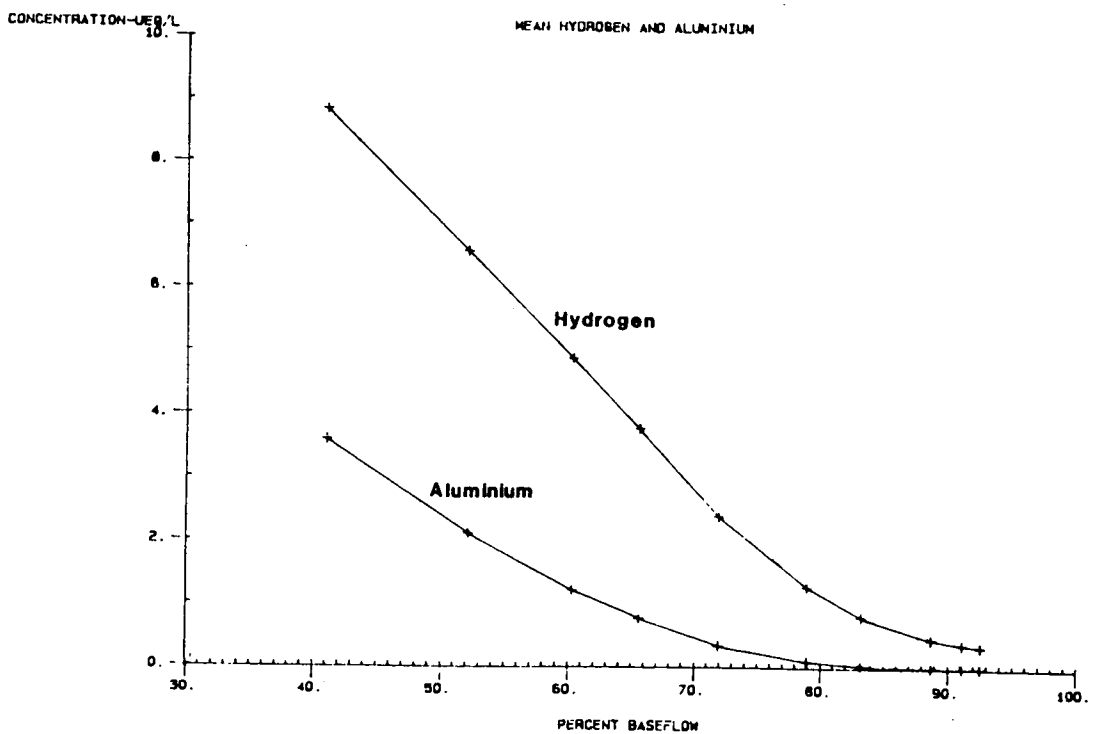


Figure 5(a) Sulphate deposition history used as input for the MAGIC reconstruction of pH in the Dargall Lane moorland catchment.

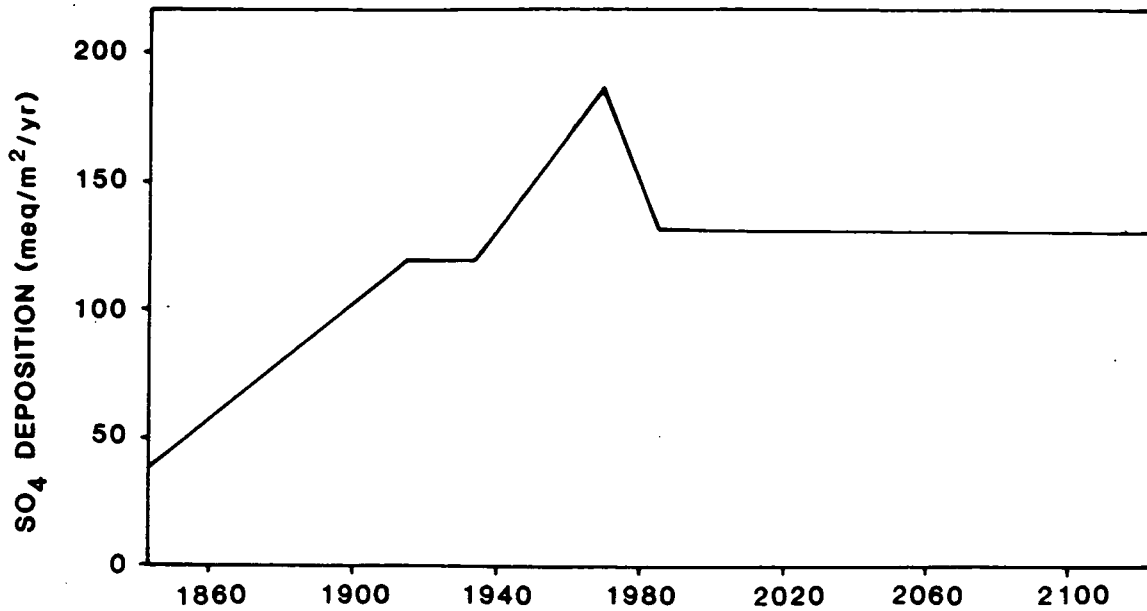


Figure 5(b) Simulation of the pH of streamwater in the Dargall Lane moorland catchment assuming three sulphate deposition scenarios

- Historical levels to 1984 and constant 1984 levels thereafter (see Figure 5(a))
- Historical levels to 1984 and 1984 levels reduced by 50% by the year 2000 and constant thereafter
- Historical levels to 1970 and constant 1970 levels thereafter.

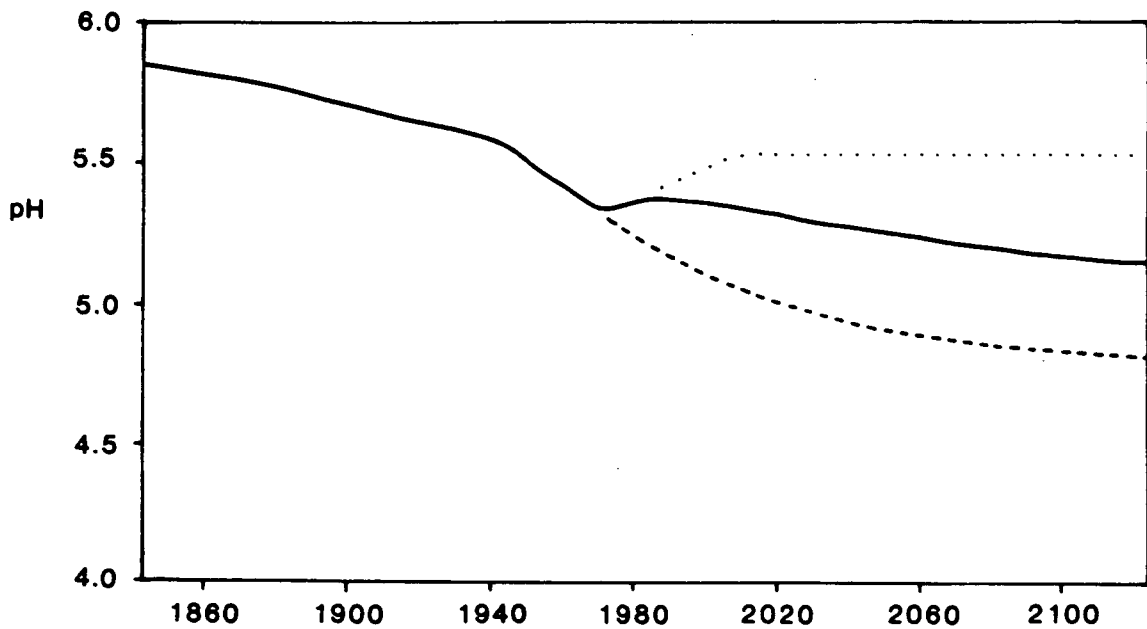


Figure 6(a) Simulation of the pH of the streamwater from the Dargall Lane catchment comparing the moorland catchment response assuming Figure 5(a) deposition rates (—), the effect of 14% additional evaporation following afforestation (.....), the effect of 14% additional evaporation plus 15% additional input of natural sea salts following afforestation in 1985 (-----), and the effect of 14% additional evaporation plus 30% additional input of natural sea salts following afforestation in 1985 (- - -).

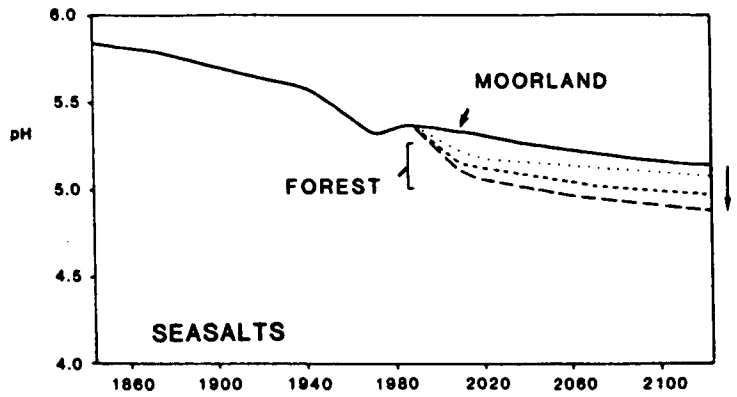


Figure 6(b) Simulation of the pH of streamwater from the Dargall Lane catchment comparing the moorland response (—) to the forested catchment response assuming increased evaporation (-----) with different levels of pollutant scavenging (....., 20% additional sulphate,-----, 40% additional sulphate,---, 60% additional sulphate).

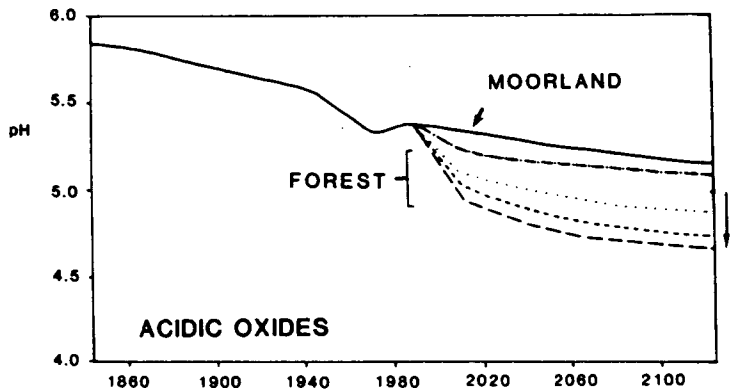


Figure 6(c) Simulation of the pH of streamwater from the Dargall Lane catchment showing the moorland response (—) and the combined effects on the forested catchment of increased evapotranspiration, increased scavenging of natural sea salts, and various levels of increased scavenging of pollutant inputs (-----, zero additional pollutant scavenging,....., 20% pollutant scavenging,-----, 40% pollutant scavenging,---, 60% pollutant scavenging).

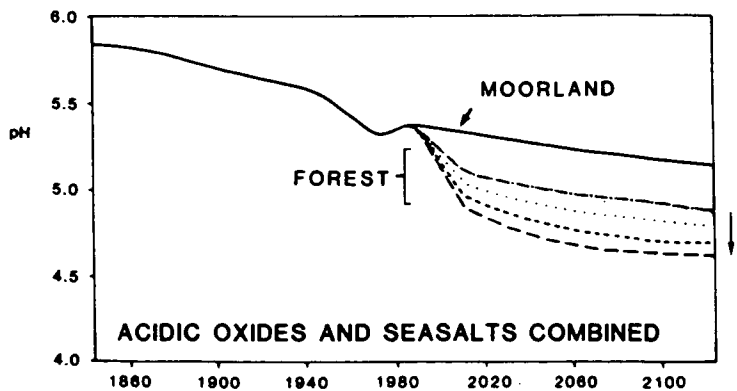


Figure 7(a) Simulation of the pH of streamwater from the Dargall Lane moorland catchment assuming sulphate deposition patterns (shown in Figure 5(a)) modified by various factors to reproduce a range of loading conditions (ie from pristine to heavy pollution).

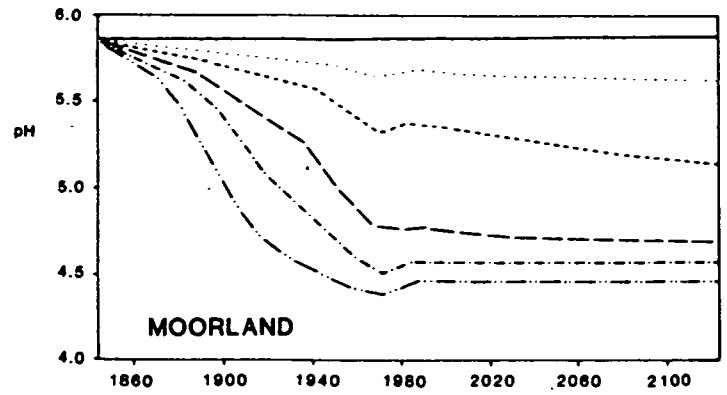


Figure 7(b) Simulation of the pH of streamwater from the 'forested' Dargall Lane catchment assuming afforestation from 1884 onwards and sulphate deposition patterns (see Figure 5(a)) multiplied by various factors to reproduce a range of loading conditions from pristine to heavy pollution.

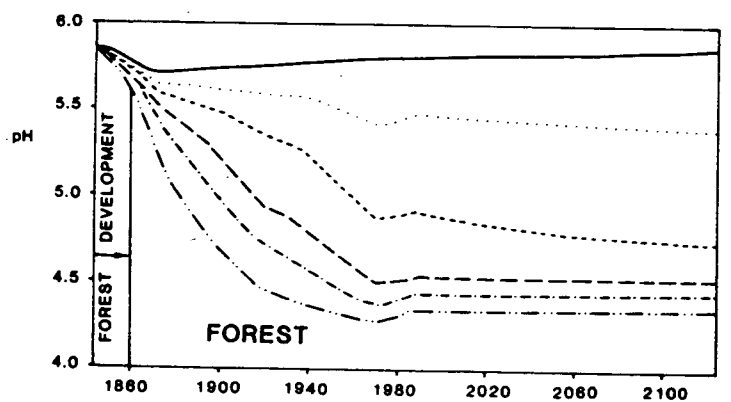
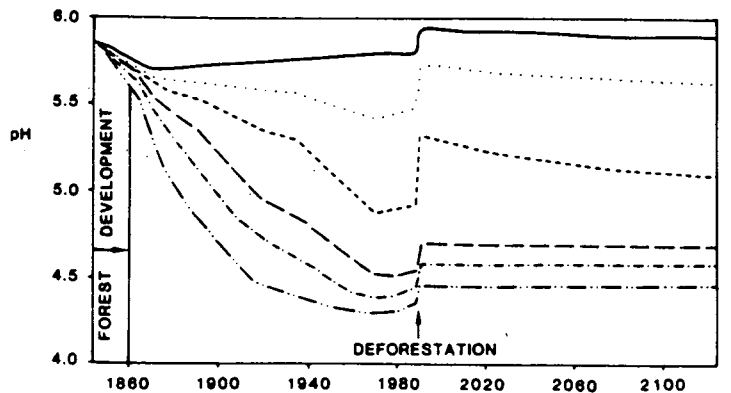


Figure 8 Simulation of the pH of streamwater for the Dargall Lane catchment assuming afforestation from 1844 and deforestation in 1990.



- | | | |
|-------|---|-----------------------|
| — | Background rates | (pristine conditions) |
| | 0.5 x Figure 2a deposition concentrations | (low pollution) |
| ----- | 1 x " " " " |) intermediate |
| - - - | 1.5 x " " " " |) pollution |
| ----- | 2 x " " " " |) heavy |
| ----- | 3 x " " " " |) pollution |

CATCHMENT CLASSIFICATION

K R Bull & R G H Bunce

SUMMARY

Classification methods are useful for ordering large amounts of data into convenient groups or classes. When applied to environmental data they can provide a framework for future ecological studies as well as offering a means of measuring and predicting environmental changes. This paper explores the approaches used in the past in various environmental classifications and examines their application to practical problems. The classification of lakes and river systems have, to date, proceeded along several lines employing chemical, ecological, and environmental data bases. We will present examples and discuss their applications. The use of whole catchments for river and lake classifications is particularly valuable when considering acidification. Within a catchment, several environmental factors may contribute to acidification, which can be included in the classification system. The availability of data is often a limiting factor for classification. Nevertheless, if the classification method is sufficiently flexible, it can make use of readily available data, and then later include additional information as it is produced. Geographically too, a classification system obtained for small areas, may subsequently be extended to include other catchments of interest. The detailed chemical and biological measurements on a few catchments can be selected from the classes and used to estimate values for much larger areas.

INTRODUCTION

Resources for survey are more limited now than ever before, and it is therefore impossible to measure all the variables that could give an exact answer. Instead, compromises have to be made in order to produce estimates of the required parameters with acceptable accuracy and with minimal cost. Progressively, the models and data bases which have been developed in recent years reflect such limitations; they are often descriptions of small parts of the environment chosen for specific studies. However, to use such data efficiently they need to be capable of being fitted within a framework so that the study areas can be seen in perspective with the overall environment. Such a framework will then provide the means for selecting truly representative samples, and for extrapolating the data already collected to other parts of the environment. Furthermore, additional data sets can be added at a later stage.

Environmental classifications, together with their associated data bases, can provide the necessary framework. Environmental strata may then be identified which can be used in many different ways but making the best use of the limited amounts of data that can be incorporated. There is an analogy between stratified environmental sampling and the identification of social strata in human populations. However, the environmental application is still relatively novel, whilst social strata are widely recognised as a useful tool for predicting human behaviour, as seen by the efficiency of the advertising industry in its prediction of human taste.

ENVIRONMENTAL CLASSIFICATIONS

The stratified approach has been used widely in other studies, but has only recently been developed for ecological survey (Bunce *et al*, 1983). Multivariate methods are used to analyse large arrays of environmental attributes rather than detailed measurements of a few variables. The data

fed into the analysis are designed to provide a summary of the areas investigated, giving a classification and hence a stratification base which holds correlations over a wide range of ecological variables. The strata are derived from attributes collected from relevant data bases, and, in most cases, will correlate sufficiently highly with measured parameters in the field, to enable predictions to be made. Although associated with environmental factors, the attributes are not necessary causal in the traditional ecological sense. So, for example, altitude may be associated with certain soil types or climate patterns, as well as correlating with a range of other ecological factors - it is therefore an important integrating attribute.

For the initial environmental classification National Grid squares, either 1 or 10km squares, have been used to define areas for classification as a convenient sample unit and for subsequent mapping. In the initial stages, a large number of randomly selected squares are classified using predominantly map derived attributes. The attributes can, however, be recorded from any unit which is suitable for a particular study. For example, as described below, the unit may be a river or a catchment. A large number of attributes are measured at this stage. The classification procedure uses all these attributes, but a smaller number of important attributes is then identified and subsequently applied with greater efficiency to the classification of the entire area (Bunce, 1984; Smith, 1982). The resulting classes form the required framework for planning the collection of field data; this data may be used for predictive calculations or to assess current baselines.

There are two broad methods of analysis used in classifications.

(1) Divisive methods, eg Indicator Species analysis (Hill *et al*, 1975) and TWINSpan (Hill, 1979), have been more widely used than other methods for a number of practical reasons (Pielou, 1969; Gauch & Whittaker, 1981). They are hierarchical, generating a family tree of classes with recognisable inter-relationships. These analyses are also convenient as they identify the key attributes used in the classification which may then be applied as described above. Ordination techniques may prove helpful, in combination with ISA or TWINSpan, for looking at data and identifying relationships between classes.

(2) Agglomerative methods. The recent work by Moss (1985) describes the results using the K-means procedure, which produced classes for his data which were equally useful or more efficient than those derived using ISA and TWINSpan.

The methods described have been applied at various geographical levels, regionally, nationally and internationally. Several regional studies in Britain, such as those in Cumbria (Smith, 1982), the Scottish Highlands (Bunce *et al*, 1984a) and the Culm measures in north Devon (Bunce, 1984; Brandon, 1986) have proved useful planning tools in looking at current land use and for calculating future potential. Nationally, ITE has applied the method to Britain (Bunce & Heal, 1984; Bunce *et al*, 1984b), deriving 32 land classes from attributes identified from maps of 1228km² OS grid squares covering Britain. This classification has formed the basis of models predicting environmental changes in Britain (Bunce *et al*, 1984b).

CLASSIFICATION OF RIVER AND LAKE SYSTEMS

In recent years, an increasing amount of effort has been spent on classifications of aquatic systems using several different approaches. Maitland (1979) has discussed the value of a synoptic data bank for Great Britain which would provide a scientific background for the interpretation and classification of aquatic ecosystems. Basic data has been tabulated on

all river systems in the UK marked on 1:625000 OS maps. Cluster analysis using ordination methods, enabled representative sites of 16 clusters of standing waters and 14 clusters of running waters to be surveyed. Regional surveys, such as that on the freshwaters of Shetland (George & Maitland, 1984), have employed similar methods.

River plant communities have formed the basis of a trophic ranking system developed by the Nature Conservancy Council (Holmes & Newbold, 1984), whilst a TWINSpan analysis of plant communities at over 1000 sites on more than 150 rivers identified four main classes, and 56 minor classes (Holmes, 1983). This is not an environmental classification of rivers but rather a classification of biological field data; other environmental data collected in the field or from maps is to be the subject of future analysis (Holmes & Newbold, 1984).

Macroinvertebrate communities have been used by the FBA and ITE to classify British rivers. As well as cataloguing the biological resources of each water course and reappraising the NCC's range of rivers scheduled in the Nature Conservation Review, it is seen as creating a framework for a better understanding of river ecology (Wright *et al*, 1985). The project also aims at examining the chemical and physical features of sites and their biological communities, to see if environmental variables can be used to predict the presence of certain macroinvertebrates.

The above projects are all aimed at defining zones along rivers or occasionally defining sets of standing water bodies. The idea of classifying zones along rivers was described for fisheries management purposes in Europe and North America by Hawkes (1975). Although the idea of zones is sometimes a useful one, in many instances it is valuable to consider the surrounding land which provides the source of drainage water to lakes and rivers. For the impact of acid precipitation in particular, the surrounding geology, soil, topography and land use are likely to be very important, so classification of entire catchments are essential.

CATCHMENT CLASSIFICATIONS

Stream and lake catchments are attractive units with which to work. They can easily be defined from contour maps, and they have proved convenient for modelling the movement of water and material carried by it; they have identifiable sources (eg springs, rainwater) and sinks (eg outflow, evaporation, underground aquifers). In addition, the terrestrial environment may be considered as a series of adjoining catchments covering 100% the total land surface.

The classification of river catchments was carried out on a large scale in the ITE Upland Land Use project in Cumbria in the 1970's. 19 Cumbrian valleys covering areas of 10 to 10km² were described in terms of the classification of the 1km² squares of their surface area. Lowland valleys were therefore identified by the high percentage of lowland class squares, and upland valleys by the presence of upland class squares. Although there are limitations to using this approach for small catchments it is an attractive proposition for large river catchments as the river classification can run concurrently with the classification of the standard 1km² squares for other purposes. Classification of some river catchments in SW England are being made in this way (Brandon, pers comm).

For many purposes there is a need to work on a much smaller scale. This is particularly true of catchments studied in acid precipitation investigations. Modelling projects are often concerned with areas in the order of 1km² or less, and chemical monitoring of streams and tarns shows

that it is often the smaller, upland waters that are the most acid. To continue using a grid square (raster) approach, much smaller squares are needed. Alternatively, the catchment itself can be used as the study unit, essentially a vector description of a map area. This has disadvantages for many computations, but gives good resolution for small catchments.

Charter (1984) has used catchment areas in her classification of 76 small tarns in the Lake District, though this is not aimed at classifying tarns for acidification purposes. Catchment sizes range from 1.5 to 50000 hectares. An ITE project on acid deposition and groundwater, which is run in collaboration with BGS, specifically aims at looking at small, uniform, stream catchments (Bell, pers comm). Instead of classifying large numbers of catchments and selecting representatives of the classes, however, the project chooses its own classification scheme based upon geology, soil type, land use and acid input; catchments have then been selected to fit the scheme. This procedure is analogous to the gradient analysis of Whittaker (1960), which pre-dated the use of computers and multivariate analysis. Of the possible 120 factorial combinations, not all are represented in the areas chosen for study ie SW Scotland, the Cheviots and the Lake District. Field surveys of the catchments chosen are intended to provide information on stream and base-flow chemistry, invertebrate populations and physical stream characteristics.

Our own work on catchments in NW England (Bull & Hall, 1986), has classified catchments defined by sampling points monitored by the NWWA; these are part of their investigations on the effects of acid precipitation in the area. Initial classification of 40 tributaries of the rivers Esk and Uddon using information from OS, soil, geology and rainfall maps produced an initial clear division of catchments into upland classes and lowland classes. The classes correlated well with the chemistry and biology measured by the NWWA. When the classification was extended to include other Lake District catchments monitored by the NWWA, size became the main important separating attribute, and most Esk and Uddon catchments fell into the small classes; these were subsequently subdivided into upland and lowland classes as before. Further extending the classification to include catchments from the southern Pennines results in geological differences featuring in the classification. This work will be extended over the next 3 years to include catchments from Wales, Scotland and other areas of England. We aim to derive a framework of classified catchments which will put those catchments which are currently the subject of detailed investigations, into context with other less studied areas.

A classification system on its own will not provide all the answers. In planning, it is seen as a powerful supplement to, rather than a replacement for, traditional plan-making processes (Bunce, 1984). In the modelling context, it may provide a framework for extending the results obtained from detailed models to broader areas of Britain.

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Workshop Reports

QUESTION 1: Can we resolve and classify soil/land use types so that they can be accommodated as sensitive determinants rather than the confounding factors that they currently represent in catchment models?

SUMMARY OF GROUP REPORTS

The need for a classification

There was general agreement that classification was a useful first stage and basis for sampling representative catchments, and as a means for distinguishing main environmental differences between or within catchments. Some participants also felt that the classification should relate directly to the sensitivity of catchments to acidification.

Attributes for classification

There was general agreement that soil and land use are useful attributes for classifying catchments. Most participants identified other attributes which should also be taken into account, including the following:

1. soil type (soil series);
2. geology (mineralogy of parent material);
3. topography (including size);
4. atmospheric inputs (climate, deposition);
5. hydrology (drainage characteristics);
6. land use;
7. vegetation.

The lack of independence between vegetation, soil and land use was noted, as was the deficiency of land use as a suitable variable for mechanistic models. However, the key variables that caused differences in sensitivity to acidification and which are used in dynamic models are implicit in the classes of a classification; they need to be explicit before they can be used. The importance of soil properties such as base saturation, weathering and cation exchange capacity were stressed.

There were also suggestions that analysis of the interdependence of the attributes used in the classification would identify those which were the most useful, and that the main classifications could be refined and sub-classified if necessary. Although examples of simple land use types were suggested, it was stressed that there was a need for an agreed classification of land use/vegetation types. Nevertheless, there were limitations in the available map data bases at regional and national scales.

Some participants felt that information from reconnaissance stream sampling surveys (Ca, pH, alkalinity, aluminium) would provide a simple, cost effective way of classifying susceptibility of a catchment, and indicate the sensitivity of regions. Economic and aesthetic/conservation dimensions should also be considered for inclusion.

The data bases

The inadequacy of current data bases which could be used for classifications was appreciated, and the need for them to be improved was stressed, especially by extending them to upland areas. It was suggested that more effort should be made to integrate and standardise existing data bases. However, the completion of such data bases is a costly exercise, and might be more justified on wider environmental grounds than

for the evaluation of acidification. It was also suggested that soil, geology, hydrology and land use data might be combined to define sensitive areas, and that comparisons should be made with biological data bases as these become available.

The use of models and the importance of soil parameters

While it was generally agreed that models could be of use to test classifications or the importance of key variables, it may be important to weight particular variables, eg carbonate, which may have a predominating effect. There was some general agreement on the soil variables needed for mechanistic models. Cation and anion exchange capacity, base saturation, cation absorption and desorption, weathering rates, mineral reaction rates, soil thickness and permeability were all identified as being important variables which needed to be measured and assessed for use in models.

The value of surveys was identified for relating catchment classes to water quality and for measuring field attributes for modelling. However, while it was suggested that the classification might be used to extrapolate the results of modelling, it was pointed out that experimental results should be used cautiously in field situations where the effective reaction surface may be very different from the bulk property. In particular, there is a need to assess variations within catchments as well as between them.

Some participants felt that the present models were too simplistic, and that more effort should be put into the construction of more sophisticated models. In such models, soil variables should operate in conjunction with climate, geology and land use.

Remote sensing

It was suggested that remote sensing could be a useful tool for classifying land use, especially where the current data base for land use was poor.

Use of existing studies

It was stressed that it was important to concentrate on existing studies for future work on classification. In particular, similar and different catchments might be identified in this way as well as recognising important omissions. Such use of classification would open up the way to model comparisons and a clearer definition of sensitive catchments. Indeed, regional surveys of existing study sites could be used to measure the attributes required for modelling. Existing studies could also be useful as a means of concentrating multidisciplinary effort, as well as for measuring such variables as weathering rates.

MAIN CONCLUSIONS AND RECOMMENDATIONS

1. Classifications are needed as a first step in identifying broad environmental variation.
2. Other attributes than soil and land use are required for classification, and these attributes were identified by the Workshop.
3. Data bases should be improved by integrating, standardising and extending those already existing.

4. Models should be used to test classifications and the importance of key variables.
5. Following classification, models may be applied to regional studies.
6. The Workshop felt that there was general agreement on the soil variables needed for mechanistic models.
7. Remote sensing should be investigated for classifying land use.
8. Existing studies should be used, where possible, for future classification work.

QUESTION 2: Can we quantify the role of nitrogen compounds in the acidification of catchments?

SUMMARY OF MAIN POINTS

Nitrogen contribution

Nitrogen compounds are potentially important in acidification processes, but the acidification of soils and streamwaters should be considered separately.

Dry deposition

Although wet deposition rates of nitrogen compounds were quantifiable, not enough was known about dry and occult deposition because they were difficult to measure. New methods and/or a network of sites were suggested for providing baseline information. The interaction between vegetation and dry deposition was also identified for further study and quantification.

Nitrogen transformations and hydrogen ions

The Workshop identified the need for further work on nitrogen transformation processes. Data were required for sources, sinks and transformations, and it was suggested that there should be a review of the published work in this area.

Transformation processes for further study may be summarised as follows.

1. Denitrification. We know little about ammonia fluxes, their magnitude or their origins. The fluxes of other nitrogen containing gases are also not known.
2. Cycling within vegetation and the effect of changing vegetation. Some vegetation/soil systems seem to produce excess nitrogen, but we do not know the mechanisms.
3. Nitrogen fixation. The significance of such fixation in acidification processes is uncertain, and is difficult to measure.
4. Organic nitrogen. Importance of organic nitrogen inputs to acidification of soils and waters was not known, and it is suggested that a desk study to clarify this issue should be carried out.
5. Biologically mediated nitrogen transformations. The impact of land use and management (eg livestock impacts and vegetation changes) on these transformations needs evaluating.
6. Drainage effects.
7. Organic matter oxidation.
8. Proton transfer. In general, there is a need to rethink the nitrogen cycle, fluxes and transformations in terms of hydrogen ion (proton) transfer. The proton balance is more important than the nitrogen itself, and there is a need for research to link the nitrogen cycle with streamwater acidification.

Land use management and upland studies

The Workshop stressed the important effects on nitrogen budgets arising from

land use and land management practices. Fertilizer inputs are the most important source of acidifying nitrogen in the lowlands, and animal grazing has also been shown to have important effects. There is little information on such effects in the uplands, and the need to transfer the attention of research from the lowlands to the uplands was stressed.

Temporal variations

In stressing the importance of temporal changes, the seasons, crop cycles and storm events were identified. The factors controlling the variations associated with these changes are unclear, and it was urged that process models should include a temporal factor.

Models

Although most participants suggested that models should be developed, the difficulties of constructing detailed models for nitrogen were noted. While simple models could be constructed using inputs and outputs, more reliable estimates could be obtained from models including processes such as mineralisation, uptake and denitrification. The importance of organic nitrogen, fungi and existing acid conditions in the uplands were also noted. Such models would require detailed studies on nitrogen budgets, and might also involve comprehensive balance studies on a small catchment.

Existing knowledge and the co-ordination of research

The Workshop felt that we should use our existing knowledge of the nitrogen cycle to identify the areas relevant to acidification, and to identify subjects for future research, possibly using existing catchment studies as a focus for field studies. Some participants believed that there was a need to integrate nitrogen studies and to co-ordinate present and future research.

MAIN CONCLUSIONS AND RECOMMENDATIONS

1. Although wet deposition is quantifiable, we need to know more about dry and occult deposition.
2. More work is needed on nitrogen transformation processes and several such processes were identified by the Workshop.
3. There is a need to rethink nitrogen fluxes and transformations in terms of hydrogen ions.
4. It was agreed that land management practices have important effects on nitrogen budgets, but there is a need for more information on the effects of land use management in the uplands.
5. Temporal changes (eg seasons, crop cycles and storm events) should be studied.
6. Models should be developed, although it was felt that detailed models may prove difficult to construct.
7. Existing knowledge should be used to narrow the areas relevant to acidification and to identify subjects for future research.

QUESTION 3: What can we say about trends in catchment acidification and the responses of various kinds of catchment over time to systematic reductions in gaseous emissions of SO₂ and NO_x? Can we model these trends and the proportion of the acidification due to deposition?

SUMMARY OF MAIN POINTS

Evidence for acidification of freshwaters and soils

The participants of the Workshop believed that the best evidence for long-term acidification is that from diatom remains in lake sediments. While some participants felt that this evidence was conclusive, others felt that some results still need explanation and noted that, per se, this evidence does not give the cause of acidification. It was reported that there was evidence that some fisheries records show reductions in fish populations had taken place and this provided circumstantial evidence for the acidification of some freshwaters. These changes, however, were often confounded with land use change.

It was agreed that data on water chemistry provided little, or only weak, evidence for acidification, mainly because of the inadequacy of historical data. There was also little evidence for soil acidification as a result of acidic deposition, although, there was some evidence of afforestation causing acidification.

It was noted that the timescale of observed changes matched the increase in SO₂ emissions in the past. However, while models can reproduce the long-term trends in acidification, there are distinct uncertainties in making future predictions. It was recommended that all stratigraphic data on lake acidification in the UK should be collated to assess the evidence for acidification from natural causes and from emissions. The data bases held by ADAS, the Macaulay Institute and the Soil Survey of England and Wales should be examined for evidence of soil acidification.

Response to emission control

In discussing the responses to emissions, the non-linearity of the relationship between emissions and depositions was emphasised; it is difficult to link these 2 groups of variables. The importance of meteorological influences were also stressed as a major factor affecting deposition and it was suggested that there was a need for more information on deposition processes and models.

The need to use models to predict the response of catchments to changes in the rate of deposition was identified, and it was pointed out that freshwaters were likely to respond more quickly than soils to reductions in emissions. A stratification/modelling exercise to rank sites in order of their response to emissions was suggested.

Recovery processes

Recovery processes were identified as requiring more study. The role of chemical and microbiological recovery processes needs evaluation, and the role of natural acidification requires estimation.

Models

In general, the Workshop believed that models were an important step in predicting the response of catchments to depositions and emissions. Current models were sometimes crude, but modelling is in its infancy and existing models should be developed and expanded. Factors suggested for inclusion in models included meteorology, natural acidification processes, land use/management and episodic events. By inclusion of such factors in the models, catchments shown as unresponsive to reduction of emissions could be tested against alternative land management techniques. Because of the uncertainties attached to predictions from models, critical validation against existing data sets and the uncertainties of data inputs were essential.

Soil variables

The Workshop drew attention to the importance of soil variables in the acidification process. The need for information on weathering, base saturation, ion exchange capacity, ion absorption was stressed. It was suggested that the inclusion of such variables in models will help to identify those which are important. If information is collected for a range of typical catchments, such information might be applied, through the use of models, to the classification of catchments for wider use. It was recommended that catchment sensitivity maps might be drawn up using soil characteristics in order to seek UK sites where soil acidification may have occurred.

Classification

It was felt that classifications would be useful, for a variety of purposes, eg to give better baseline data on the distribution of acid waters, to identify the parameters for monitoring and modelling, for constructing sensitivity maps, and to classify catchments in terms of rate dependent processes.

Long-term monitoring

The Workshop emphasised strongly the need for long-term monitoring studies, and that these should be both chemical and biological. While it was recognised that monitoring would present logistic problems, the use of classifications to select representative sites for monitoring was recommended. It was stressed that data interpretation should not be separated from the monitoring itself, and sufficient support should be made available to ensure the maximum benefit from the data collection. The importance of acid events or episodes in determining stream biology was indicated, together with the need for automatic sampling.

No more recommendation was made of a suitable body to undertake such a monitoring commitment, but it was suggested that the research councils were perhaps the most appropriate organisations. The need to establish and maintain analytical quality control was highlighted.

Other work

The Workshop believed that there was a need to extend the work on palaeoecology to a wider range group of catchments, including unpolluted areas and other taxonomic groups. There was a need for a multidisciplinary approach to catchment studies and acidification problems. Fish/aquatic species sensitivity maps should be constructed at a local scale to detect where species may be absent for reasons other than acidification.

MAIN CONCLUSIONS AND RECOMMENDATIONS

1. It was agreed that the evidence for acidification in freshwaters is strongest in lake diatom records. Fisheries evidence is circumstantial, and chemical evidence is weak.
2. It was agreed that there was little evidence for soil acidification.
3. There is a need to link emissions to deposition rates. The importance of meteorological factors in this linkage was noted.
4. More work is needed on soil recovery processes.
5. The Workshop saw models as important for predicting catchment responses. Current models can reproduce past trends, but there are uncertainties in prediction. Models should be developed and expanded, and various additional attributes were suggested for inclusion in such models.
6. Soil attributes are important, and there is a need for information on these for modelling.
7. The Workshop identified several important uses for classification.
8. There was a strongly felt need for long-term monitoring. In particular an organisation or organisations should be identified as being responsible for such monitoring. Adequate analytical quality control was stressed.
9. Work on palaeoecology should be extended.

Appendix 1 Current Projects

AN APPRAISAL OF THE EFFECTS OF VARIATIONS IN ACID DEPOSITION ON GROUNDWATER IN DIFFERENT GEOLOGICAL ENVIRONMENTS IN NORTHERN BRITAIN (EEC CONTRACT ENV.870 UK (H))

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This project is a reconnaissance study largely of upland streams in Northern Britain draining catchments of different land uses, soils and bedrock geology. The criteria being assessed are groundwater chemistry and populations of aquatic invertebrates. The project consists of two parts: a) a Regional Study, and b) a Synoptic Study.

In the Regional Study, sites were selected in the Lake District, Southern Uplands and the Cheviots using 4 main sets of criteria, stratified as follows:

- a) Bedrock geology: granite, greywacke, calc-alkaline volcanics, shales, sandstone.
- b) Soil type: rankers, brown forest and gleys, peaty podzols and peaty gleys, peat.
- c) Land use: forest, rough grazing.
- d) Total average acid deposition 0.5-0.9; 1.0-1.4; 1.5-1.9 kg H⁺ ha⁻¹ annum⁻¹

The sites were all above 1000 ft OD, in areas free of glacial deposits, where possible, and in streams draining an area of uniform geology.

Of the 120 factorial combinations of the main criteria, 37 of them were met in the 55 sites sampled. Sampling was carried out during June 1985 when water samples for chemical analysis were taken simultaneously with biological samples. The water alkalinity, pH, specific electrical conductivity, water temperature and several other parameters were measured at each site. A second round of sampling, this time for water only, is planned for a period of low flow later this year.

The biota have now been examined, and species of Hirundinea, Gastropoda, Bivalvia, Malacostraca, Tricoptera, Plecoptera and Ephemeroptera have all been identified.

The water samples have been chemically analysed by ICP-OES and automated colorimetry for NO₃, SO₄, Cl and a wide range of major, minor and trace elements. The data have been put on computer and statistical treatment is currently in hand. There are wide pH and alkalinity ranges within each bedrock category and the lowest pH measurements were taken in the granite and sandstone categories, concomitant with low alkalinity, low concentrations of Ca and Mg and high levels of Al. There is an apparent correlation between low pH and low acid input in 3 of the bedrock categories.

In the Synoptic Study 4 areas of diverse combinations of bedrock, soil, land use and acidic deposition, where low alkalinity groundwaters are

likely to occur, each approximately 20 km x 20 km, were selected. These are:

- a) Galloway in an area of greywacke, mudstone and granite.
- b) Innerleithin over greywacke, mudstone and minor granites.
- c) Cowal over Dalradian metasedimentary rocks with some Upper Old Red Sandstone.
- d) Speyside over drift-covered Moine quartzites, granite and Dalradian metasedimentary rocks.

The Galloway and Innerleithin areas both contain several sites in the Regional Study for cross-reference. Water samples from springs, streams, rivers and wells were taken at 767 sites. No biological samples were taken, but all other parameters measured in the Regional Study were repeated. Chemical analysis of the samples is complete and statistical treatment of the data is in hand.

ALUMINIUM MOBILISATION DURING THE INTERACTION OF ATMOSPHERIC DEPOSITION WITH ACID SOILS.

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Aluminium solubility in soils has been shown to depend on the details of soil composition as well as on the more obvious pH factor (ref.1). Clay content, organic matter and the total anion concentration are the composition variables that drive the solubility, cation exchange, organic complexation and hydrolysis equilibria to determine aluminium concentration in a given system at equilibrium. Real soils are rarely at equilibrium. Variable water flow rates and variable salt contents are implicated in determining the actual aluminium concentration found in pore waters. These systems are being studied in mini-lysimeters in the laboratory.

The variation of soil properties both vertically within a profile and across a land surface would be expected to modify the aluminium concentrations in waters in different parts of a catchment, including its surface drainage. Detailed hydrological pathways are likely to be as important as soil properties in this respect (ref.2). Classification of catchments for acidification studies must take account of both hydrology and soils and should depend on whether one is looking for gross neutralisation of incoming acidity or for quality of drainage waters.

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CHEMICAL INPUTS FROM PRECIPITATION AND THEIR EFFECTS OF THE CHEMISTRY OF A CATCHMENT AREA. DOE CONTRACT PECD 7/10/53-66/83

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The small catchment (0.66 km²) under study is sited on Beacon Hill in Leicestershire. It is situated on an old volcano, on granitic bedrock, and rises several hundred metres above the East Midlands countryside. It is vegetated with stands of coniferous and mixed deciduous woodland and areas of bracken/moorland species. The freshwater system under investigation comprises a series of small ponds and streams which have a common confluence at the base of the catchment.

In order to examine the relationship between inputs from rainfall and the chemistry of these freshwaters, a monitoring programme has been established. Rainfall and freshwater samples are collected on an event and weekly basis from a number of rain gauges and pond and stream sites on the catchment area. These samples are subsequently analysed for volume and chemical composition.

Frequent monitoring has revealed the existence of spatial and temporal variation in the chemistry of waters flowing from the atmosphere to the freshwater system. Not only is there a variation in concentrations of different ions within a single rainfall event, but the concentration of each individual ion also varies markedly from event to event. Indeed a large proportion of the total annual loading of ions such as hydrogens, sulphate, nitrate, nitrite, chloride and ammonium may be contained within a relatively small number of rain events.

A seasonal variation in freshwater chemistry has also been established in the freshwater sites and is influenced by the proportions of water emanating from ground water and surface/soil flow sources. High concentrations of inorganic aluminium (2-4 mg l⁻¹) and low pH values (3.5-4.5) exemplify the "winter" state whereas low aluminium concentrations and more neutral pHs are characteristic of the "summer" state of the catchment freshwaters. Superimposed on these seasonal patterns are shorter term fluctuations in chemistry which are associated with particular types of rain events, such as storms and mists and rain containing specific ionic loadings.

A spatial variation in freshwater chemistry across the catchment also exists and is related to vegetational cover, the most marked chemical fluctuations being associated with run off from coniferous woodland.

The characteristics and responsive nature of this catchment present an ideal opportunity to study the relationships not only between rainfall and freshwater chemistry but also the modifying influence of soils and vegetation and investigate the associated biology.

CLASSIFICATION AND COMPARISON OF RIVER AND LAKE CATCHMENTS USING COMPUTING TECHNIQUES.

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Freshwaters, which are being studied by the North West Water Authority (NWWA) as part of their investigations into acidified waters, are the basis

of a catchment classification system we have developed for some streams and standing waters in NW England. Whole catchments were chosen as study units with the aim of including most of the factors which may affect the acidification of these waters. An initial classification of 40 tributaries classes identified were associated with more acid waters. The classification has been extended to include other stream catchments from the Lake District and from the Southern Pennines, whilst a separate classification has been made of lake and tarn catchments from the same areas. It is planned to develop a classification system for other catchments which are being studied, chemically and biologically, throughout Great Britain, especially those which are the subject of acidification studies. Such a classification will provide a framework for comparison of current studies on freshwaters and a way of relating such studies to freshwater catchments throughout the environment.

DESCRIPTIVE AND FUNCTIONAL MODELS OF THE RELATIONSHIP BETWEEN RAINFALL AND SOIL WATER TABLE

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In order to study the effects of artificial drainage on upland forest soils, soil water level and rainfall have been measured daily in a number of experiments. Each experiment comprised 36 plots varying in size from 15 x 30 metres to 45 x 30 metres; the level of free soil water was measured in 4 boreholes in each plot. A first order auto-regressive model was used to describe the response of the water level in each borehole to the series of rainfall events by the model:

$$z_t = \lambda z_{t-1} - \alpha X_t + H(1 - \lambda) - V_t$$

Where z_t is the depth of the water level in the borehole at the end of the t^{th} day. X_t is the rain which fell on the t^{th} day. V_t is an error term. λ is an index of the rate at which the phreatic surface falls, the drainage rate, (a low value means rapid drainage), α is an index of the reciprocal of the specific yield, (a high value means small drainable pore volume). It also includes the intercepted fraction since the rainfall reaching the forest floor differs from that falling outside the forest by an amount equal to the interception loss. H is the asymptotic depth to which the phreatic surface apparently decays in the absence of rain. A combination of the estimated parameters yields the notional computed infiltration at saturation, K , in centimetres of rainfall per day in the equation $K = (1 - \lambda)H/\alpha$. Maximum likelihood estimates of the 3 parameters can usually be successfully obtained in peaty gley soils but where rates of change are too large (brown earth soils) or too small (deep peats) the method is not successful. Experience has shown that even small differences in land drainage characteristics can be detected and that the method can be used to predict levels of free soil water in response to given rainfall events.

Though descriptive models provide an efficient means of describing data sets and detecting differences which arise through experimental treatments they do not help to elucidate the processes involved. For this reason a finite element model has been developed which describes water movement in drained forest soils by taking a grid of 1600 elements (squares or rectangles) to represent a two dimensional cross section of a drained soil. An equation of state, involving all soil parameters (which can be different in each element) as well as pressure, volume and flow of water, is solved for each element through time, taking into account the effects of

neighbouring elements. This results in a two dimensional representation of a phreatic surface and the effects of soil type and topography can be studied in relation to variable rainfall inputs. The model was developed because of the lack of objective information about the effects of drainage on thin sloping soils. The model has already helped in understanding the processes involved and in demonstrating what is likely to happen under a range of conditions (eg slopes of different gradient and soils of different thickness). However, it is stable only under a fairly narrow range of conditions and for some parameters (eg conductivity) does not work with realistic values. A copy of FEMWATER, a finite-element model developed by Yeh & Ward at Oak Ridge Laboratory, has been mounted at Alice Holt and will be modified to deal with the conditions in which we are interested.

FRESHWATER LOCH SURVEYS IN SCOTLAND

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The survey and classification of lochs by the Nature Conservancy Council serves 4 main purposes:-

- a) to identify representative examples of loch types in order to protect them;
- b) to assess the extent of change and damage to lochs in an area;
- c) to identify sites which are vulnerable to change and damage by such processes as eutrophication or acidification;
- d) to provide baseline data against which future survey results can be measured.

Before the conservation value of the lochs in an area can be compared they are classified by their macrophyte communities. This classification can usually be linked with the trophic status of the water bodies. Representative examples meeting other nature conservation criteria are then recommended for protection. Macrophyte data for open waters all over Britain are now being combined for analysis by the TWINSPAN program making easier the national site comparison and selection.

A second classification based on physical characteristics of the lochs and their catchments is still being developed which could back up the first aim, a), and which could also be based to identify vulnerable sites, aim c). For the purpose of identifying sites vulnerable to acidification some data are easier to use than others. The proportion of granite and other base-poor geology and the proportion of peatland or conifer forest in the loch catchments, the buffering capacity of the water, the water through-put of the lochs as well as the water pH and aluminium levels are among the parameters to measure. There would appear to be scope for combining data and sharing results with other organizations in this field.

The initial regional surveys are rarely able to identify precisely any changes which have occurred. There have usually been no comprehensive surveys in the past with which to compare present data. It is intended that the current surveys should provide the baseline data against which the results of future surveys can be measured. It is therefore very important to identify now the parameters which will be most useful in identifying such processes as acidification. The recognition of important indicator species with narrow ranges of tolerance is seen as an important next step in this work, which I would wish develop further in these surveys.

THE EFFECT OF ACID RUN-OFF ON THE CHEMISTRY OF STREAMS IN NORTH WEST ENGLAND

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Chemical aspects of river water quality have been examined in the (W. Cumbria) River Esk and Duddon, at other sites in the English Lake District, and more recently in the South Pennine area.

The investigation follows concern from local anglers over declining fish runs in the Esk and Duddon since the mid 1970's culminating in a serious fish mortality in June 1980, extending over several days, in high river flows following a long dry period. Over 100 adult fish were affected, mainly fresh run sea trout, some salmon, and a much larger number of juvenile salmonids.

Automatic monitoring equipment has been in operation since May 1983, and a complete record of pH, temperature and river flow variations was obtained in September, 1983, during a second, albeit less serious fish mortality, involving mainly adult fresh run sea trout.

Since that time no further fish mortalities have been observed in these catchments. The monitoring has been extended to include conductivity and automatic samplers, which are triggered by a rising river level, to take water samples for calcium and aluminium analysis in particular. Fish counters are also now in operation on both the River Esk and Duddon.

A striking correlation between river pH and river flow has been found at both continuous monitoring sites, which appears to be independent of rainfall pH (as measured at the downstream River Esk site).

A number of sites have been identified where fish are known to have been present up to around 1970, but are no longer present. It is thought likely that these fish were killed during intense acid episodes during the mid 1970's. Preliminary analysis of results from the continuous monitors suggests that conditions are improving relative to 1983.

Remedial measures being pursued include stream liming on selected marginal spawning streams, and an increase in agricultural liming on the River Esk catchment only. Investigations have demonstrated that there was a substantial drop in the amount of lime applied to the catchment since the liming subsidy ceased in 1976. Calculations suggest that this provided a major part of the calcium present in the main river, and may well have helped to prevent mortalities of fresh run fish. This type of liming would not, however, benefit many of the spawning tributaries which are above limable areas.

BIOLOGICAL STUDIES IN CUMBRIA AS PART OF NWW ACID RAIN PROJECT

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Acidification-related mortality of salmonids in the River Esk in 1980 prompted an investigation into the fish stocks, benthic macroinvertebrates and water chemistry of 75 upland stream sites of salmonid nursery stream type within the Lake District National Park, split equally between the River Duddon catchment, the River Esk catchment, and a group of other hill stream sites. Subsequent biological work has extended site coverage over all likely sensitive Cumbrian catchments, and sought to provide more

detailed description of linear (upstream/downstream) and seasonal trends in some of the most affected areas. The latter work has included trial fish stocking and caged fish exposures.

The impact of liming in Spothow Gill (Esk tributary) on the biota, including stocked trout, is being monitored and liming trials in other catchments are planned.

Biological surveys, including gill netting and electric fishing tributary streams on some highly acidic tarns with past records of fish stock showed eg. a thriving trout population in Seathwaite Tarn but no evidence of fish stock in Levers Water.

Generalising on our stream findings, those unexpectedly with salmonids absent or at exceptionally low densities are encountered in the upper parts of the drainage systems of the western mountain mass of the Lake District, particularly in the upper Duddon and Esk and some nearby catchments. These streams are in areas of high rainfall (>2200 mm/year) with underlying rocks of the Borrowdale Volcanic series, mean pHs of 5.6 or less, and mean calcium level approximating 1-2 mg/l Ca.

Notable sites outside this limited area with markedly acid restricted faunas are the upper River Glenderamackin (mean calcium only 0.6 mg/l) and the upper reaches of Blea Beck (in the region of Shap granite).

Our detailed study of selected acid streams with severe faunal restriction has frequently shown marked downstream chemical and faunal changes over very short distances, associated with catchment changes such as the onset of drainage inputs from improved grazing land at the upper limits of settlement in the valleys.

We have noted the value of acidification indicators such as Baetis, and quite strong correlations between measures of juvenile salmonid population densities and chemical determinands of acidification.

ACID PRECIPITATION - VEGETATION - ORGANIC SOIL INTERACTIONS

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Experiments with simulated precipitation and Sitka spruce branches or 8-y pot-grown trees and with Calluna vulgaris plants have shown that acid deposition enhances leaching of base cations. The effect is significant for Mg, Mn, K and Na, and, especially, for Ca. For Ca, K and Na, leaching from Sitka spruce with H₂SO₄ was significantly higher than leaching with HNO₃. Provided dry deposition was excluded, the neutralisation of H⁺ balanced base cation leaching, confirming an ion exchange mechanism. It must be assumed that a corresponding H⁺ flux is transferred by the root to the soil. For simulated acidified mist, H₂SO₄ caused more leaching of base cations from Sitka twigs than did HNO₃, particularly for K and Mg.

Increased deposition acidity increased base cation leaching from upland moorland and forest surface soils and lowered the solubility of TOC, Al and Fe, leading to horizon acidification and reduced CO₂ production. Sitka litter leachate was shown to reduce bacterial activity significantly in underlying mineral soil when incoming precipitation was acidified. This effect could not be explained in terms of pH reduction. After prolonged exposure to simulated 'acid rain', bacterial counts were lowered in a

forest surface soil. From our experiments the dominant effect on microbial activity appears to be the long-term soil acidification effect in surface horizons, rather than any short term direct effect.

Field studies at Glendye and Glenbuchat have shown substantial retention of deposition nitrate inputs by sphagnum and Calluna. Surface organic horizons also retain nitrate. This explains the low stream nitrate levels over much of the year. Bracken appears to be a particularly efficient collector of atmospheric pollutants and bracken throughfall has exceptionally high levels of sulphate.

Any model system on a catchment scale must include possible soil acidification effects of acid deposition. These would have a direct acidification effect upon the drainage water pH and, in susceptible soils, an indirect effect through reduced microbial respiration. In the long term, possible effects of accelerated peat accumulation must also be considered.

STUDIES OF GEOCHEMICAL WEATHERING RATES BY CATCHMENT STUDIES AND THEIR SIGNIFICANCE IN ACID RAIN RESEARCH

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The chemistry of precipitation and of the main streams and minor tributaries in two upland catchments in Northeast Scotland have been monitored for two years. Soils in one catchment, Glendye, are predominantly evolved from granite, in the other, Peatfold, Glenbuchat, from the more basic quartz-biotite-norite. Weathering rate calculations show that the surface soils at Glendye are at or near the end of the period of postglacial weathering where leached calcium may be substantially replenished by mineral weathering.

In both catchments, water only becomes acidic during storm events when lateral flow downslope through organic surface horizons makes a greater relative contribution to total discharge. It has been demonstrated using equilibrations in controlled atmospheres that the normally high pH of the river water at or near base flow is a result of outgassing of CO₂ obtained from microbial activity and root respiration in soils. This process is reduced in importance during prolonged heavy rain, so that water remains more acidic.

Climatic variation from year to year has been seen to be very important. November 1984, for example, was abnormally wet, and led to correspondingly abnormally high acidic peaks at the very high discharge prevailing. The water pH trough was a whole unit lower than normal for autumn storms.

Factors which increase the water flux flowing laterally through organic horizons may substantially modify water chemistry. These include indurated horizons, placons (iron pans) and frozen soil horizons. When snow melt is not very rapid and not confined to surface horizon flow by frozen sub-surface horizons, acidity pulses may not be observed in the stream during melt. Snow cover over unfrozen soil may apparently protect the soil from freezing by subsequent very low air temperatures.

All our results to date suggest acid rain is likely to affect water acidity only via the effect it may have upon soil pH, unless inputs direct to lakes or streams are significant. This is unlikely for streams. Blown snow may

add significantly to the direct input of acid to lakes.

Sulphate anion exchange is more important to Glenbuchat than Glendye. Sulphate is leached at the latter catchment, where B horizons of soils on lower slopes are already sulphate saturated, and retained at Peatfold. Sulphate exchange for hydroxide leads to neutralization of H^+ from cation exchange sites and base cation retention. Thus sulphate saturation of anion exchange sites leads to base cation leaching.

CURRENT RESEARCH ON SHALLOW GROUNDWATERS AND RIVER BASEFLOW RELATING TO ACID RAIN AND ACIDIFICATION

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D G Kinniburgh

Hydrogeochemical research is being carried out on shallow groundwater systems in the following areas:

1. The susceptibility of UK groundwaters to acid deposition

Available data on low pH, low alkalinity groundwaters throughout the United Kingdom has recently been reviewed and compared with a classification of the bedrock geology, to identify those areas of the country which are most susceptible to acid deposition (Kinniburgh and Edmunds, 1984; Edmunds and Kinniburgh, 1986). Although groundwaters in the major aquifers are generally alkaline and well buffered, shallow groundwater and river baseflow in several formations, e.g. Millstone Grit, Lower Greensand, Permo-Triassic sandstone, Lower Palaeozoic and Pre-Cambrian, have low alkalinity and may be susceptible to acidification. (DoE support).

2. Attenuation of acidity in the unsaturated zone

The fate of atmospheric inputs of acidity and rates of movement of solutes in the unsaturated zones of poorly buffered lithologies are being investigated to assess the longer term impact of acid deposition on water supplies. Interstitial water profiles and mineralogical data are being obtained from core samples to depths ranging from 6-30 m in Tertiary and Quarternary sands and sandstones, and the Sherwood Sandstone. (DoE support).

3. Regional geochemical surveys of shallow groundwater and river baseflow

Hydrogeochemical sampling of representative geological areas, 200-300 km² is being carried out to test the sensitivity of different lithologies to acidification. A database is being established for each area including geological, land use and chemical information (20 inorganic species). Studies completed in Speyside, Cowal and Border regions. (part EEC funded in collaboration with ITE). A hydrogeological and chemical study of groundwater contributions to Loch Fleet catchment has been carried out under contract to CEGB.

4. Experimental studies of the acid buffer capacities of British soils and rocks

The objectives are to determine the principal factors controlling the kinetics of H^+ uptake by selected British soils and rocks, to develop a chemical model describing this uptake and to define a set of standard experimental conditions for comparing the acid susceptibility of different soils and rocks (Kinniburgh, 1986). (EEC support).

References:

- KINNIBURGH, D.G. & EDMUNDS, W.M. 1984. The susceptibility of UK groundwaters to acid deposition. 211 pp. Report to Department of the Environment.
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ATLANTIC SALMON PRODUCTION IN SCOTTISH CATCHMENTS

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Salmon populations are widespread in Scotland. The results of extensive enquiries on salmon distribution, field-survey work and catch analysis make the project of value in determining the impact of acidification and changes in land use on the wild salmon populations of Scottish catchments.

Salmon Distribution

Up-to-date information for the whole of Scotland has been collected from primary sources (knowledgeable locals) and mapped at a scale of 1:250,000 (Gardiner and Egglisshaw, 1986). The information indicates that salmon are absent from many streams as a result of the presence of physical barriers (such as waterfalls) which prevent the upstream passage of adult salmon.

Map Analysis

Various stream and catchment attributes are known to influence the densities and growth rates of salmon parr. Of general importance are stream size and altitude. Good progress is being made on estimating the surface areas of running water (in classes of stream width and altitude) which is reported to be,

1. physically accessible to adult salmon and contain salmon,
 2. physically accessible to adult salmon but not contain salmon,
 3. physically inaccessible to adult salmon,
- in each catchment.

Field-Survey

The classes of stream have provided a framework for the selection of sites for field-survey. It is expected that, for a reliable assessment of the effects of land use and acidification, a larger number of sites will need to be visited within the stretches of stream which are physically accessible to adult salmon. So far, the fish populations have been sampled at a total of 127 sites.

Catch Analysis

Detailed information on salmon catches has been collected since 1952 by the Department of Agriculture and Fisheries for Scotland. The decline over the period 1952 to 1981 in the annual salmon catch of some catchments has been found to correlate well with the amount of upland forest, most of which has been planted in the past 30 years (Egglisshaw, Gardiner and Foster, 1986). In addition, the data on catch and stream surface area are being examined together for other evidence of local influences affecting the productivity of catchments over the last 30 years.

References

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WELSH WATER AUTHORITY

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Analysis of rainfall collected weekly at 46 sites throughout Wales during 1984 has shown that its quality varies from >4.7 near the coast to 4.3 in central and east Wales. Higher pH values near the coast are associated with high chloride levels, reflecting the influence of the sea. In contrast, high 'excess' sulphate levels are obtained to the east and south of the country.

The areas most vulnerable to acification are those with hard rocks and base-poor soils receiving high rates of deposition. In Wales, much of this area has been planted with conifers over the past fifty years or so and this has exacerbated the acidification of surface-waters. Studies of fish and macroinvertebrates have shown that the ecology of streams and lakes reflects water quality.

Over the next 3-5 years detailed studies of 12 catchments draining into Llyn Brienne are being conducted with the support of funds from the Department of the Environment and Welsh Office. Five of these, including moorland, conifer and deciduous wooded catchments will act as controls. Seven catchments will undergo land-use treatments, including liming, ploughing, tree planting and forest clearance.

Comprehensive meteorological data are being collected using an automatic weather station in addition to wet and dry deposition. Stemflow, throughfall and soil water are being collected within sample plots of each catchment. Apparatus for continuous monitoring of streamflow, pH, temperature and conductivity are operational in each catchment. Total rainfall is also being continuously monitored by tipping-bucket type raingauges which trigger liquid autosamplers at the onset of each rainfall 'episode'. Water samples collected in this way for laboratory analysis complement those determinands continuously monitored in the field. The fish and macroinvertebrates fauna of these streams are being studied concurrently.

Additionally, laboratory based studies on fish toxicity and the speciation of aluminium in these waters are supplementing the field investigations. These studies are being conducted by the Welsh Water Authority (including sub-contracts to several University departments) and the Institute of Terrestrial Ecology, with the assistance of the Forestry Commission and the Institute of Hydrology.

c) High sulphate depositions (Loch Ard, Galloway).

Commenced 1985.

3. a) To determine the process by which coniferous afforestation can increase stream acidity (and Al, Mn etc).
- b) To assess the liming requirements for acidified upland lochs (Loch Dee project).

This work involves the comparison of forest and moorland catchments within the same area (Loch Ard, Loch Dee) and between areas of high (Loch Ard sites) and low (North-west sites) acid deposition to separate the "forest" effect from the acid deposition effect.

4. To study the ecological effects of different forestry practices in acid and alkaline catchments.

During the coming decades large areas of forest will be felled and replanted in Scotland. The following management options will be investigated:

- a) Complete clearfell - Burn 10 (Loch Ard) (Acid pH 4.4)
- Kirkton (Balquhidder) (Alkaline pH 7)
- b) Bank clearance - Burn 7 (Loch Ard pH 4.6)
- Corrie (Loch Ard pH 6.5)

A 20-25m swathe will be cut along the stream bank and effects on chemistry, hydrology and invertebrates (acid streams) plus fish (alkaline streams) will be studied.

5. Identification of the key processes and assessment of their relative contribution to surface water acidification in relation to rainwater chemistry and soil status (eg Acid rain, sea-salts, soil oxidation, hydrological pathways).
6. To study the chemistry, in particular aluminium speciation, pH, calcium and dissolved organic matter, and its toxicity to aquatic organisms in vulnerable streams; with references to intensity and duration of episodes. Various sites throughout Scotland.

Collaborative projects - Freshwater Fisheries Laboratory (F.F.L.)

1. Loch Dee (Galloway) with Solway River Purification Board and Forestry Commission.
2. Loch Ard Studies with Forth River Purification Board; Forestry Commission; Macaulay Institute for Soil Research (M.I.S.R.).
3. Rannoch Streams (for Department of the Environment); Tay R.P.B.
4. Balquhidder (Kirkton) - Consortium of groups.
Water Quantity - Institute of Hydrology (I.O.H.).
Water Quantity - F.F.L.; Forth R.P.B.; Strathclyde Regional water Authority; M.I.S.R. plus A.Q.C. on chemical parameters with W.R.C.

5. Surface Water Acidification Programme. (S.W.A.P.).
- a) Pristine sites - North-west Scotland - F.F.L.; Highland R.P.B.
 - b) Transitional - Mharcaidh (Cairngorms) - F.F.L.; M.I.S.R.;
I.O.H.; Imperial College.
 - c) Acidified - Loch Ard sites - F.F.L.; Forestry Commission;
Imperial College; Forthe R.P.B.; M.I.S.R.

Contracts - Freshwater Fisheries Laboratory (0796) 2060
Co-ordinator - Dr D E Wells.
Site Manager - R Harriman - chemistry
 B R S Morrison - biology

CLOUD PHYSICS GROUP UMIST

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The group at UMIST has been carrying out a programme of cap cloud microphysical measurements at Great Dun Fell, Cumbria for over a decade. Included in this programme have been measurements of precipitation and turbulent deposition rates of cloud water to the hill surface. Recently, the group have become involved in collaborative work with ITE and AERE Harwell and also CERL with an aim to understand the role of the aqueous phase in the oxidation of S(IV) to S(VI) and associated water acidifying mechanisms.

An air flow model of the hill incorporating cap-cloud (generally applicable to hills of aspect ratio <0.3) has been developed. The atmosphere can be divided into up to three layers, thus allowing for the effects of stratification on the local windspeed which can be very important. This in turn affects the turbulent deposition rates considerably. Measurements of windspeed over the surface of the hill show good agreement with the model. This model is used as a basis for theoretical studies of deposition rates of cloud - water/pollutants and also the washout process in which high level precipitation falls through the cap cloud and scavenges cloud water on its way to the ground.

A model has been developed which predicts the masses of sulphate and hydrogen ions deposited as cloud parcels move over the hill and predicts that typically the greatest rates occur on the leeward side of the hill. The surface roughness length has been measured experimentally from the vertical wind gradient. The washout model has been extended to make predictions of the masses of pollutants in the rain hitting the ground and predicts that both the maximum rates and their position is dependent on hill size and the windspeed. Field measurements have been made and are in good agreement with this model.

Substantial measurements have now been made of SO_2 , O_3 , H_2O_2 , NO_x and rain/cloud water composition at various altitudes on the hill and combined with the meteorological/microphysical data now available routinely are providing considerable insight into the rate of oxidation of SO_2 in solution and the rates at which pollutants are removed from the atmosphere.

2. The surface chemistry of clays and soils

Clays and soils play an important role in modifying water chemistry through their ability to exchange ions from solution for the clays own ions. This process of ion exchange has been studied extensively at IH as part of the NERC geochemical cycling project, initially in relation to estuarine studies but now with emphasis on freshwater systems. Three main lines have been developed to date.

- a) A new variable (notional interfacial content) has been introduced to define rigorously the cation exchange system.
- b) A new method has been developed for the analysis of clays and soils
- c) An electrostatic model, based on Gouy-Chapman theory has been developed to describe ion exchange reaction.

INCREASED STREAMFLOW AFTER CLEARFELLING A SPRUCE PLANTATION AT KERSHOPE FOREST, CUMBRIA

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Introduction

When upland forests are clearfelled there is an increase in streamflow but the size of the increase depends on the nature of the forest, the soil and the climate. We felled a Sitka spruce (*Picea sitchensis*) plantation 20 m tall and three 2 hectare plots of a drainage experiment and compared the water balance with a control plot before and after felling. (Changes in the chemical composition of the water from its receipt as precipitation to its departure as drainflow were monitored by the Institute of Terrestrial Ecology).

Method

We measured precipitation (P) outside the forest in 5 gauges including one at ground level which caught 2 percent more on average than gauges 30 cm above ground level. The results for the ground level gauge are quoted below. Throughfall (T) was collected in 90 cylindrical gauges of 11 cm diameter and stemflow (S) was collected from 30 trees. Interception loss was calculated as the difference $P-(T+S)$. The plots are contiguous, clearly defined by perimeter drains and the soil is a peaty gley with a watertight clay base; other losses of water are therefore thought to be mainly by transpiration and evaporation from the soil. There is no ground vegetation under the spruce stand.

Results

In 1981 and 1982 (before felling) interception loss accounted for 38 percent of the precipitation, drainflow for 49 percent and transpiration and other losses for 13 percent (Table 1).

Table 1. Water balance (mean of 3 plots). Units mm.

Year	Precipitation P	Throughfall T	Stemflow S	Drainflow (Runoff) R	T+S-R	P-R
1981	1403	740	122	692	170	711
1982	1568	841	137	769	209	799

Felling of the 3 plots of Table 1 took place during 1983 leaving a ground surface virtually devoid of live vegetation throughout 1984 but covered in a thick layer of dead branches and tops. In 1984 drainflow represented 66 percent of precipitation, the other 34 percent being ascribed mainly to evaporation from the harvesting debris and soil surface (Table 2).

Table 2. Water balance of plots before and after clearfelling.

Year	Precipitation P	Mean of 3 plots felled during 1983		Control plot (not felled)	
		Drainflow R	P-R	Drainflow Rc	P-Rc
1982	1568	769	799	710	858
1983	1278	622	656	462	816
1984	1259	837	422	433	826

1985 data not yet available

The water balance of the control plot during 1983 and 1984 was affected by the rainfall being lower than in 1982. Total evaporation and other losses (P-Rc) were slightly reduced but represented an increased proportion of precipitation. Drainflow was markedly reduced in absolute terms and as a proportion of precipitation. If this effect is allowed for in the 1984 results for the felled plots, the "expected" drainflow if felling has not taken place would have been 477 mm. Thus felling may have increased drainflow by 360 mm.

Conclusions

The increased drainflow resulting from clearfelling forest at Kershope is towards the upper end of the range of values in world literature. This was expected because of the high interception loss from the plantation, because the vegetation change affected the whole plot, and because the plot is watertight.

CEGB CATCHMENT STUDIES

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The Technology Planning and Research Division of the CEBG has undertaken a number of studies of acidic catchments. Whether they have been "acidified", and if so by what, is another question. The current state of these projects and their documentation is summarised briefly below.

1. Snake Pass

A rough catchment budget was calculated for 2 basins in the headwaters of the River Derwent in Derbyshire on the basis of one year's data (1977). A report has been issued.

2. Tillingbourne

A 5-year study of the passage of SO_4^{2-} , NO_3^- , NH_4^+ , Cl^- , organic material and H^+ through a 1 km² forested catchment on Leith Hill, Surrey, was performed between 1977 and 1982. Measurements taken included bulk precipitation, throughfall, soil water and stream water from various sources. To date, 12 papers and reports have been issued.

3. Cuttiemore Burn

The Cuttiemore Burn is the main feeder stream of Loch Grannoch, Galloway. A 3-year study measuring rain inputs and stream outputs of all major cations and anions on a weekly basis was mounted between 1979 and 1982. The aim was to assess the influence of forestry on stream chemistry. The forest was newly-planted (1977) and the effect was slight, but it may be worth re-examining the Burn now the forest is older.

4. Loch Fleet

Loch Fleet is a small loch in Galloway where a large-scale acidity mitigation project is underway, funded by the Electricity Supply Industry and the National Coal Board. Although not primarily designed as a catchment study, various sub-catchments have been identified and catchment budgets could be calculated. The project involves numerous sub-contractors and various catchment treatments and publications should be forthcoming shortly.

RESEARCH RELEVANT TO ACIDIFIED CATCHMENT CLASSIFICATION AND MODELLING

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The projects described are not directed solely at the acid rain problem but are believed to be relevant to the workshop themes.

A number of projects under the collective title of Synoptic Limnology have the general objectives of the 'long term study of British freshwater ecosystems with a view to classifying them, describing their variety and, eventually, to understanding the structure of their communities and the habit requirements of different organisms'. For a number of these, the

Project Leader is Peter Maitland (same address). I am directly concerned with the following:-

1. Distribution of freshwaters in Great Britain. An account of the numbers and characteristics of standing and running waters, classified by Hydrometric Area.
2. Hydroclimate. This is concerned with the physical aspects of the synoptic work, particularly the generalisation of existing data. It is based on the premise that a river basin should be treated as a single system so that the physical factors controlling species distribution and the fate of material entering the river system can be predicted. Algorithms for driving variables (streamflow, temperature, etc) are being developed as well as models for predicting the response of both standing and running waters.
3. Streamflow and hydrochemistry. This is a joint project with Mr Lin Yaoming who has since returned to Peking. The first part is concerned with how the water composition of runoff (the proportions of base and quickflow) varies with the state of the catchment as measured by antecedant rainfall and evaporation and has been tested on the River Tyne in East Lothian. The project goes on to consider whether the relation between water flow and dissolved load at the catchment scale can be predicted knowing the source of dissolved material and the time during which reactions take place.

WATER QUALITY MODELLING RESEARCH

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Water quality modelling at IH has developed considerably in recent years with a wide range of applied and theoretical studies. Many projects have been established with water authorities, government departments, universities and organisations such as UNESCO and the Royal Society.

The research has developed from real time forecasting models to investigating river basin management problems and, most recently, to an extensive programme on acidification processes in catchments.

A system of flow gauging and water quality stations with data telemetered to a central mini computer has been developed for several UK river basins (eg. Bedford Ouse, River Thames) and mathematical models of flow and quality have been installed on a central computer to provide real time forecasts for operational management. Such models have also been used to assess the effects of changing low flow conditions and effluent discharge rates on stream quality. Also a model of algal growth and transport along river systems has been developed.

River basin studies have been undertaken to investigate the movement of nitrates in catchments and future nitrate levels in rivers. It is important to recognise the non-conservative nature of nitrates in such a study and take into account processes such as denitrification. Similarly in a study of heavy metals in the River Tawe the interactions between sediments and the water column has proved to be an important aspect. A model of heavy metals in the Tawe has been developed to investigate the problems of effluent disposal and the various methods of meeting river quality objectives.

The most recent area of research has been to develop models for predicting the effects of acid deposition. This research has been undertaken for the EEC and the Royal Society and involves establishing a number of catchment studies in the UK and using the data to develop catchment models. A range of modelling techniques are being applied. This includes, for the hydrological description-time series analysis, and both lumped and distributed catchment models; for the chemical process description-time series analysis, separate dynamic and steady state process models plus combinations of both types. Eventually, it is hoped to couple hydrological and chemical process models together. Catchment studies have been established in Scotland (Loch Dee - Galloway and Alt-á-Marquaie - Cairngorms) and Wales (Plynlimon and Llyn Brianne). In addition statistical techniques are being applied to long term records in Norway, Sweden, Scotland and Wales to assess trends in acidification. A large number of factors can affect catchment acidity such as deposition levels, soil type, underlying geology, land use and management practices. An investigation of long term changes may reveal useful information on the relative magnitude of these factors.

Thus a wide range of modelling techniques and catchment studies are available at IH. These will be developed further and will be applied to new emerging problems. The problems of acidification will undoubtedly continue and become more important as the effects and process involved are better understood. It is proposed that the IH contribution could follow our current lines of research and make use of the catchment hydrochemical models to assess the relative impact of point and non-point sources of pollutants. Considerable information is already available for catchments such as the River Thames, the River Tawe, Loch Dee and Plynlimon and these catchments would form the basis of our research.

Appendix 2 UK Catchment Studies

	Catchment(s)	Organisation	Contact name(s)
ENGLAND	Esk & Duddon	NWWA, Warrington NWWA, Carlisle FBA, Windermere ITE, Monks Wood	D. Crawshaw R. Prigg D. Sutcliffe K. Bull
	Lake District various	FBA, Windermere NWWA, Warrington NWWA, Carlisle ITE, Monks Wood	D. Crawshaw R. Prigg K. Bull
	Slapton Ley	Sheffield University Oxford University	S. Trudgill T. Burt
	Bicknoller Combe Somerset	Oxford University	T. Burt
	Southern Pennines	NWWA, Warrington	D. Crawshaw
	Beacon Hill	Loughborough University	V. Black
	Bondhay Dyke Nr Sheffield	Sheffield University (Geography Dept.)	S. Trudgill
	Macclesfield	Manchester Poly	
	Merevale Warwickshire	Lanchester Poly	J. Dearing I.D.L. Foster
	Narrator Dartmoor	Plymouth Poly (Geography Dept.)	A. Williams L. Ternan
	Exe	Exeter University (Geography Dept.)	D. Walling
	Highland Water New Forest	Southampton University (Geography Dept.)	A. Gurnell
	Tillingbourne	CERL	R. Skeffington
	Coalburn	IH	D. Robinson
	Kershope	Forestry Commission ITE	G. Pyatt J. Adamson

WALES	Plynlimon	IH	G. Roberts
		ITE	M. Hornung
		BGS	B. Reynolds
			N. Breward
	Beddgelert	ITE	M. Hornung
		Forestry Commission	
SCOTLAND	Llyn Brianne	Welsh Water	A. Gee
		ITE	M. Hornung
		Forestry Commission	P. Stevens
	Various	Welsh Water	A. Donald
	Llanbrynmair	IH	G. Roberts
	Nant y moch	IH	G. Roberts
SCOTLAND	Balquidder	IH	J.R. Blackie
		DAFS, Pitlochry	R. Harriman
		Macaulay	
		Forth R.P.B.	
	Loch Ard	Macaulay	
		DAFS Pitlochry	R. Harriman
		Forth R.P.B.	
	Loch Fleet	CERL	D. Brown
		Macaulay	
	Ochils	Stirling University	I. Grieve
	Glendye	Aberdeen University	M. Cresser
	Glenbuchat	Aberdeen University	M. Cresser
	Various	Macaulay	Pedology Dept.
	Loch Dee	SRPB	Bill Welch
	DAFS, Pitlochry		
	Forestry Commission		
Allt a Mharcaidh (SWAP)	DAFS	R. Harriman	
	IH	L. Morris	
	Macaulay		
All	DAFS, Pitlochry	R. Gardiner	
Lochs Rannoch, Ard + 2 W. Scotland catchments	DOE, Pitlochry	S. Hogg	
		J. Foster	
N.W. Scotland (SWAP)	Highland R.P.B.		
	DAFS, Pitlochry		
S. Scotland + N. England streams	ITE	G. Bell	
		M. Hornung	
	BGS	P. Allen	
		M. Edmunds	

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