Hydrological pathways and acid episodes in the Coalburn catchment

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Abstract

Hydrological pathways and episodic stream acidification were investigated by monitoring water quality in the Coalburn catchment during the later stage of canopy closure. Coalburn is a long-running experimental site, almost completely covered by a commercial coniferous plantation (part of the Kielder Forest in northern England). Regular sampling, event sampling and continuous monitoring were used to establish an extensive water quality data-base between 1993 and 1997.

Cloud mist and precipitation at Coalburn are slightly acidic and the catchment can receive moderate levels of dry and wet acid deposition when the winds have tracked from an easterly direction. Coalburn streamwater chemistry displays well-buffered base-flows and acid episodes during high flows. Duration-frequency-magnitude analysis of the Coalburn acid episodes reveals they were less frequent than expected but had a longer duration. The acid events exceeded environment quality standards for freshwaters: pH and aluminium concentrations suggest a toxic impact on freshwater biota. However, the elevated calcium concentrations and presence of humic substances reduce the biological impact.

The chemical signatures and variations in solutes were identified and used to postulate the causal mechanisms of the hydrochemical response and to produce the conceptual Coalburn runoff model. Mixing modelling was then applied to introduce a robust analysis into the process and produce the simplified Coalburn Model of acidification. Broadly, the Coalburn hydrochemical response can be explained by pre-event water sources and 'normal' catchment processes. However, during extreme events catchment conditioning and event-water can also influence the response.

In improving knowledge of the likely water quality effects of coniferous plantation afforestation, the Coalburn study has contributed to calibrating the temporal and spatial variability of headwater acidification (and hence risks). This allows policy makers and environment managers to make informed decisions about land use/management and to apply the precautionary principle; the research findings were used to suggest a basic policy framework and protocols for catchment assessments to manage acidification issues through the cropping cycle within a headwater catchment.

Publications

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S. Mounsey author of the water quality subsections in:

> Robinson, M., Moore, R.E, Nisbet, T.R. & Blackie, J. R. 1998. From moorland to forest: the Coalburn catchment experiment. Institute of Hydrology Report Number 133.

Disclaimer

The opinions expressed in this thesis are those of the author and do not necessarily reflect the views, or anticipate future policy, of any of the Environment Agency or organisations quoted.

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List of abbreviations

Alk_{Gran1}	Gran alkalinity with end-point of pH 4.0.
Alk_{Gran2}	Gran alkalinity with end-point of pH 3.0.
Alk_{GranEA}	Gran alkalinity calculated using Environment Agency method.
ANC	Acid neutralising capacity.
ANC_{CBALK}	Acid neutralising capacity derived from charge balance alkalinity.
ANC_{Gran}	Acid neutralising capacity derived from Gran alkalinity.
API	Antecedent precipitation index.
AWS	Automatic weather station.
CBALK	Charge balance alkalinity.
DAC	Dry antecedent conditions.
DOC (TOC)	Dissolved (Total) organic carbon.
C_c	Conductivity from the continuous field monitor.
C_s	Conductivity derived from samples.
cSAC	Candidate special area of conservation.
EQS	Environment quality standard.
FC	Forestry Commission.
IoH	Institute of Hydrology.
LEAP	Local Environment Agency plan.
MDF	Mean daily flow.
$nmSO_4$	Non-marine sulphate.
NWW	North West Water Ltd
pH_c	pH from the continuous field monitor.
pH_s	pH derived from samples.
P_{base}	Proportion of flow attributed to the base-flow endmember.
P_{high}	Proportion of flow attributed to the base-flow endmember.
Q_b	Base-flow.
Q_s	Storm-flow.
SSSI	Site of special scientific interest.
TBR	Tipping bucket raingauge.
THM	Trihalomethane.
UKRGAR	United Kingdom review group on acid rain.
WAC	Wet antecedent conditions.

1 Introduction

The association between plantation forestry and upland catchment acidification has been a focus of much specialist scientific research. However, a direct cause and effect remains subject to discussion between researchers, reflecting the complexity of the processes that underlie catchment acidification and the hydrochemical changes that are brought about by afforestation; both of which can change in time and space. The study of afforestation and catchment acidification is still a relatively new science with a concerted research effort starting in the early seventies (McCulloch, 1997). Individual research experiments, such as Coalburn, have generally not made a paradigm shifting contribution, but have incrementally added to the overall scientific knowledge through highlighting catchment specific processes.

From an environmental management viewpoint there is a constant need to re-assess policy in light of these scientific gains and to assess the extent and seriousness of the present and future impacts of forestry on the aquatic environment. Furthermore, there is an increasing need for the environment manager to consider issues on a holistic scale and reconcile the diverse demands of environmental policy and legislation.

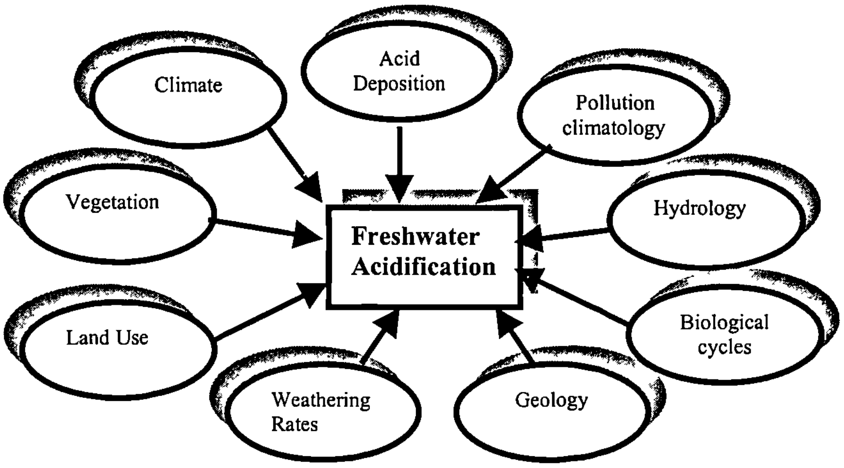
Good quality information and research for strategic planning is essential. Understanding environmental processes allows the prediction of response to a development or course of action and the risk associated with that prediction being incorrect or causing harm. The calibration of the cause-effect-risk predictions under different environmental conditions is vital if the environment manager is to make informed decisions and know when to apply the precautionary principle.

This chapter briefly reviews the historic and current information and fundamental issues pertaining to acidification and plantation forestry.

1.1 Acidification

Concern over acidified freshwaters emerged in the 1970's when almost simultaneously acidification problems were recognised in Scandinavia, USA, Canada and the UK (UKRGAR, 1990). 'Acid rain' became a prime focus of public concern, environmental research and policy making. The term 'acid rain' focused the attention to a single component of the acidification process; however, the issue is more complex and requires an holistic approach from the catchment to international scale to place the processes in context (Figure 1.1).

Figure 1.1 Factors influencing freshwater acidification



The term acidification is used to encapsulate the above processes (Figure 1.1) and is defined succinctly in the Forest and Water Guidelines 3rd Edition (Forestry Authority, 1993):

> 'A continuing loss of acid neutralising capacity manifested by increasing hydrogen ion concentrations (decreasing pH) and/or declining alkalinity.'

This may be applied to the catchment and soils or to the freshwaters in the catchment. Acid neutralising capacity is defined as the capacity to neutralise strong acids (Reuss and Johnson, 1986).

Reuss and Johnson (1986) conceptualised soil and surface water acidification in terms of capacity and intensity. The capacity referred to the total storage in the soil and with respect to acidification would be indicated by an increase in hydrogen and aluminium ions. Intensity referred to the concentration in the soil solution and surface water. The intensity component is susceptible to short-term changes (through mechanisms such as acid deposition and the mobile anion concept) in hydrogen ion and aluminium concentrations in the soil solution that are transferred to the surface water. The focus of this research programme is the mechanisms of surface water acidification i.e. the intensity component.

1.1.1 The processes of acidification

Previous acidification research in the UK uplands (including Plynlimon, Llyn Brianne and Allt a'Mharaciadh) has broadly considered acidification in terms of temporal and spatial variation. The temporal variation refers to the long and short-term variations in acidification processes, whereas the spatial component refers to the variability of acidification in terms of different soil types, geology, land-use and pollution climatology.

1.1.1.1 Temporal variations

Studies demonstrate that acidification of the British uplands is not a new phenomenon, it has occurred slowly throughout the Holocene due to slow natural processes and is associated with increased organic acidity (Neal et al., 1992; and Emmett et al., 1994). Battarbee & Charles (1994) stress natural acidification is not the cause of present day problems, but it can increase catchment sensitivity. Superimposed onto this long-term 'natural' acidification is a second phase, since the 1800's, that has primarily been derived from anthropogenically derived acid deposition.

The principal emissions responsible for acid deposition are oxides of sulphur and nitrogen, derived from burning fossil fuels; these enter a catchment through wet, dry and occult deposition processes (Reuss and Johnson, 1986). Acid deposition has accelerated catchment acidification in sensitive areas (i.e. those that tended to have a naturally acidic status) or has conditioned catchments so they are susceptible to other mechanisms (Van Breeman et al., 1982). A causal link between acid deposition and acidification of soils and runoff has been observed by Davies et al. (1992); Matschullat et al. (1992) and Driscoll et al. (1988). Although these authors cite acid deposition as the main causal factor of catchment acidification, there are few comparisons with other similar pristine sites. Thus, given the short-term records it is difficult to assess the true degree of impact of acid deposition (Driscoll et al., 1988).

Many upland catchments reported in the research literature only become acidic during short lived high-flow events, for example Plynlimon (Robson, 1993) and Llyn Brianne (Soulsby, 1992; Soulsby 1995b) and Coalburn (Mounsey and Newson, 1995). The hydrological and hydrochemical response is determined mainly by the flowpaths, storage and residence times in the catchment and the way these change during a hydrological event. Episodic acidification is ecologically potent with chronic and acute effects on the flora and fauna of ecosystems, the most severe being fish kills due to elevated hydrogen ion and aluminium concentrations. Thus, streamwater acidification is an issue of two timescales, with short-term pulses of acidity (intensity component) often superimposed onto the effects of longer term acidification processes (capacity effect) (Whitehead et al., 1988).

Research has focused on the hydrochemical processes (i.e. flowpaths, storage and residence times) that produce acid events; however, it is also important to determine the magnitude, duration and frequency of the events and relate this to the biological impact. In doing so the risk/likelihood of an event, being 'toxic' is calibrated and this knowledge is essential for policy makers and environmental managers to make informed decisions. Many studies have done this by sampling river water quality and then applying statistical techniques to estimate the characteristics of the water chemistry during extreme events. There are few studies in the United Kingdom that have long-term continuous data for catchments that exhibit acid events. Good quality continuous data are valuable as the extreme values are observed rather than estimated (with the added risk of using an inappropriate statistical technique (Robson, 1993)). Hence, the collection of continuous data allows a more detailed calibration of the water quality variation and elucidates the risks/errors in carrying out a 'normal' sampling programme. One of the objectives for the sponsorship of this research programme by the Environment Agency was to assess the value of continuous monitoring in upland catchments.

Previous studies, particularly those using continuous data, have highlighted that the major changes in upland catchment chemistry during a hydrological event are often rapid and occur at the beginning of an event. Without at least an hourly sampling frequency or continuous data there is a high probability these changes will not be captured in small upland catchments and the true variation in the catchment chemistry will remain unknown (Robson, 1993).

The issue of land-use and acidification is discussed below; however, when considering plantation forestry it should be remembered the effects upon hydrology and water quality vary in magnitude and direction as the forest ages (Robinson et al., 1998). In the early years, the cultivation and ploughing are the dominant hydrological influences. As the forest ages the drainage ditches become less efficient; the canopy's scavenging efficiency increases and the biological cycling is modified. These combine to influence the catchments' hydrological and hydrochemical response (Hudson & Blackie, 1993; Stevens et al. 1997b; Robinson et al., 1998).

Currently, there is a dearth of studies reporting the hydrological effects throughout the complete forest rotation, with the majority of studies focusing on the initial ground preparation stages or the mature crop and the felling/harvesting. These studies have estimated the effects/differences using paired catchments, a research framework that carries inherent assumptions and potential errors. The Coalburn study is relatively unique in the UK in that it is following a single catchment from moorland to afforestation and throughout the forestry rotation. This will provide valuable information to bridge this hiatus between the initial land preparation and mature forestry, and will help to calibrate the effects of processes such as canopy closure.

There is a need for long-term studies, such as Coalburn, to validate the extrapolation from short-term process studies, otherwise there is a risk that a biased view may be formed by examining a short period of a cycle (McCulloch, 1997). The fact that processes vary in time, as well as intensity, requires calibration so these changes can be successfully incorporated into policy and environmental management. For example, Local Environment Agency Plans, long-term water quality objective planning and salmon action plans need to be able to incorporate the effects of forestry for the entire rotation and to accommodate the step changes such as land preparation, canopy closure and felling.

1.1.1.2 Spatial variations

The composition of the catchment output chemistry and extent to which natural or anthropogenic acidification occurs broadly depends upon the input quality, soil type and underlying geology, all of which vary in space (Jenkins et al., 1990). The variation in water quality for any one catchment is accounted for by its physical attributes including soil depth, topography, hydrological pathways and residence times (i.e. where the water moves; how it moves; and what chemically reactive zones it encounters en-route to the stream) (Robson et al., 1992).

Rainwater is naturally acidic and the degree of buffering/addition to acidity upon entering a catchment depends on the soil and geology (Reuss and Johnson, 1986). For example, a catchment with little buffering capacity, thin soils and rapid runoff may display a direct effect between the chemistry of precipitation and streamwater (Cresser and Edwards, 1987; Davies et al., 1992).

The wind direction and duration from that direction have a significant bearing upon the input of ions from the atmosphere from both wet and dry deposition (Davies et al 1992); this effect is termed the pollution climatology. Spatially (and temporally) the pollution climatology changes according to the dominant weather patterns and with it the acid deposition that impacts on a catchment (UKRGAR, 1990). It is important that the pollution climatology is considered and linked to the catchment water quality. The study of pollution climatology has also highlighted other acidifying mechanisms such as ammonium and sea salt deposition. Ammonium can play a part in acidity; in the atmosphere it combines with acidic compounds (e.g. ammonium sulphate) and neutralises them, however, if this is nitrified when it enters the soil it will release hydrogen ions and mineral acids (Van Breeman et al., 1982; UKRGAR, 1990). Langan (1989); Wright et al. (1988); Kauffman et al. (1992) and Soulsby (1993) have observed that inputs of sea salt rich precipitation to a catchment can result in episodic surface water acidification as sodium is exchanged for hydrogen ions in the catchment soils.

Of relevance to Coalburn is previous research in catchments dominated by peat soils that have 'brown water' runoff. These contain high concentrations of dissolved organic carbon (DOC) and organic acids that can significantly lower runoff pH. Havas et al. (1984) illustrated that DOC and organic anions were responsible for seasonal and episodic variations in pH of the

River Lilan (northern Sweden), the role of strong mineral acids anions was insignificant. Acidification from organic sources is seasonal, varying with climate and plant activity (Kullberg et al., 1993). For streams draining the mid-Atlantic coastal plain Kauffman et al. (1992) observed a seasonal variation of organic acidity dominating the summer and autumn, whilst sulphates regulate stream acidity in winter and spring.

Spatial variability occurs in all the above factors. However, land-use is one aspect that can influence all of the above processes with the vegetation fundamentally modifying the quality and quantity of the incident precipitation (Newson, 1986). Change from moorland to coniferous afforestation is the most likely land-use change to occur in the uplands, and has been the focus of much research.

Coniferous afforestation in the UK has typically been concentrated in the uplands where acidic soils and acid producing moorland vegetation occur naturally. Hence, there is considerable debate over whether afforestation directly causes surface water acidification as it is difficult to separate natural and man-made acidification from the effects of afforestation (Nisbet et al., 1995). Havas et al. (1984) and Nisbet et al. (1995) suggest that acidification only occurs where pollutant inputs are high and that these inputs are the main precursor. In contrast, Ormerod et al. (1989) found a statistically significant positive relationship between the percentage forest cover and winter stream water acidity and aluminium concentrations. Department of Environment and Forestry Commission (1990) also placed strong emphasis on the role of coniferous afforestation as a direct cause of surface water acidification. This debate continues, however, making it difficult for policy makers and environmental mangers to develop national policies to mitigate the likely effects of afforestation.

The location of a catchment influences the land preparation required, such as drainage, which has implications for the routing of runoff in a catchment. Drainage/ploughing aims to remove excess soil water, improve aeration and mobilise nutrients to facilitate tree growth. However, this can also promote lateral drainage and reduce the contact time with the lower horizons that buffer acidity; this can increase the risk of acidification. Conversely, as the trees grow, their roots penetrate into the lower horizons of the soil and may promote vertical drainage of the water. This is another process contributing to the variability of forestry impacts according to the stage in the forestry cycle.

Conifers have the capacity to effectively scavenge acid pollutants from the atmosphere, compared to normal moorland vegetation, and thereby increase the input load and potential impact on the ecosystem (Department of Environment and Forestry Commission, 1990). The quantities of wet deposition are influenced very little by afforestation; however, the scavenging efficiency of a tree canopy increases dry and occult deposition compared to moorland (Department of Environment and Forestry Commission, 1990; Reynolds et al., 1989; Whitehead et al., 1988; Chappell et al., 1990). Fowler et al. (1989) reports that for Kielder Forest occult inputs of nitrogen and sulphur may be increased by between 90% and 30% respectively when the optimum conditions prevail due to the effects of afforestation.

Forest growth alters the biological cycles, consuming base cations and releasing hydrogen ions, especially in the early stages of the rotation (Ferger, 1994). This process causes a gradient of acidity in the root zone of trees from the trunk outwards (Ferger, 1994). Over time the biomass accumulates base cations and harvesting of the forest represents an export of these base cations. Successive rotations may result in an overall reduction in the soil ANC (Neal et al., 1992; Van Breeman et al., 1984; Ferger, 1994; Miller, 1985). Ferger (1994) argued the base cation consumption and export losses from catchments are greater in forests than moorland. Miller (1985) agrees, stating that the process of soil acidification is more significant than acid deposition. However, the increase in hydrogen ion concentration in the soil from root uptake does not involve the concomitant passage of an anion. The presence of a mobile anion is required to transport the protons to surface waters; this is provided by acid deposition and effective scavenging of these solutes by the forest canopy (Reuss and Johnson, 1986; Harriman et al. 1994). Consequently, it becomes difficult to tease apart the exact cause of acidification in surface waters.

Soil acidity can also be increased under coniferous stands due to the deposition of resistant pine needles which form an acid humus in the cool wet upland climates enhancing the formation of raw humus (Department of Environment and Forestry Commission, 1990; Ferger, 1994). The decomposition of the forest floor litter may be impeded further by the increase hydrogen ion deposition under conifers, decreasing the soil pH (Ferger, 1994; Bache, 1984). The formation of the litter layer is dependent upon woodland management with regard to thinning which controls the forest floor temperature and lighting; however, there are few studies on the hydrochemical effects of such silvicultural processes (Ferger, 1994).

While the above section has discussed the generic processes within the catchment, the main point is that spatially (and temporally) these processes vary, and this variation needs to be calibrated/quantified to assess the cause-effect-risk relationship. Indeed, it is clear the processes in an upland catchment in Wales or Scotland located at a higher altitude and closer to the coast will be different from those operating at Coalburn in upland northern England.

1.1.2 The effects of acidification

The second phase of anthropogenic acidification has been identified as the most potent phase in terms of ecological impact (Battarbee and Charles, 1994). The effects on streams and lakes is an issue of two timescales, with acute pulses of acidity associated with high-flow events (intensity component), superimposed onto chronic effects of acidification processes (capacity component) (Whitehead et al., 1988; Reuss and Johnson, 1986).

Brown (1983), Harriman et al. (1990), Ormerod et al. (1989) and Jenkins et al. (1990) identified the important chemical variables in assessing the effects of acidification as being the concentrations of hydrogen, calcium and aluminium ions with the following critical thresholds: pH less than 5.5; calcium less than 50 $\mu Eq l^{-1}$; and filtered aluminium greater than 50 - 80$\mu g l^{-1}$.

Ecosystems are particularly sensitive to changes in the acid status of freshwaters and the chronic biological effects of acidification include:

- Skeletal deformities in fish.
- Unsuccessful spawning and recruitment that changes the fish age distribution.
- Reduced or loss of fish populations.
- The nature, population and occurrence of the invertebrate populations are affected by the acidity status of freshwater, becoming less diverse and impoverished as acidity increases.
- Macro and micro flora are sensitive to changes in acidity.
- Linkage in the food chain are broken that can affect populations of mammals higher up the food-chain (e.g. dippers).

(Source: Ormerod and Jenkins, 1994)

At its most extreme the acute effects of acidity can result in fish kills due to the combination of the hydrogen ion and aluminium concentrations, such affects have been observed in the River Duddon and Esk in Cumbria (Crawshaw, 1985).

In general, an increase in acidification will lead to a reduction in habitat and bio-diversity that, while difficult to quantify, has a cost to society. Acidification has direct economic implications on drinking water supplies that have low pH, high concentrations of aluminium and high levels of trihalomethane (THM) precursors as it will be precluded from public supply without additional treatment. Acidification can also affect commercial fisheries with salmonids being particularly sensitive to acidity, especially at the hatching/emergence stages and acidity at these life stages can result in low juvenile recruitment (Jenkins et al., 1990; Ormerod and Jenkins, 1994).

It is important that there is an understanding of the duration, frequency and magnitude of acid episodes and particularly with reference to exceedence of the conservation objectives, ecological criteria, EU Directives and UK water quality standards. Calibration of acid events in terms of both the duration-frequency-magnitude and cause-effect-risk is essential to be able to manage the impacts of acidification in a strategic manner.

The effects of 'natural' acidity are not always detrimental, Havas et al. (1984) and Kullberg et al. (1993) suggest that brown waters have a greater ANC than similar clear water system when the $\mathrm{pH} < 5$. Indeed the biotic effects of acidification are modified by the presence of dissolved humic compounds that can reduce the toxicity of dissolved metals. For example, for the same pH, the aluminium in brown waters is not generally associated as greatly with the toxic labile (inorganic) monomeric species when compared to clear waters (Driscoll et al., 1988). However, such waters may become toxic at low pH (Kullberg et al., 1993). For a stream with the same acidity, brown waters have a greater species richness than their clear water counterparts (Havas et al., 1984; Kullberg et al., 1993). Hence, when predicting the effects of acidification upon aquatic ecosystems it is important to identify the source of acidity.

1.1.3 Management of acidification

By its very nature there are several scales of managing the acidification issue ranging from an international to catchment scale (Figure 1.1), and one of the challenges of the acidification issue is to reconcile these options within an appropriate policy/management framework.

The relationship between acid deposition and surface water acidification suggested that controlling the emissions at source was the best method of control (Battarbee et al., 1995). The United Nations Economic Commission for Europe (UNECE) set up the 'Convention for Long Range Transboundary Air Pollution' (LTRAP) to promote protocols for reduction in sulphur and nitrogen deposition. The sulphur protocol encouraged countries to reduce their sulphur emissions by 30% (from a 1980 baseline) by 1993. In 1986 the UK signed the EC Directive for large combustion plants which required a 60% decline in emissions from these sources by 2003 (Battarbee et al., 1995). However, it was realised the 30% approach was too rigid and the critical load concept was introduced; this is now firmly implanted in the UK and EU policy. A critical load is an estimate of exposure to acid deposition, below which significant harmful effects do not occur (Nilsson and Grennfelt, 1988). Maps have been prepared by the Department of the Environment Transport and Regions and the UK Critical Load Advisory Group (Battarbee et al., 1995). The critical load maps are then compared to the actual deposition rates and used to produce critical load exceedence maps. It is then a political objective to reduce the loading below that critical value for the system's healthy functioning. Areas of sensitivity in the UK include the Northern Pennines. For the UK, sulphur reductions of 70% by 2005 and 80% by 2010 (on 1980 baseline) were agreed in 1994 (Battarbee et al., 1995).

The critical loads policy has focused on reducing sulphur-dioxide emissions, thought to be the main acidifying component. Such reductions have already resulted in improvements in the acid status of many freshwaters, for example Loch Dee south-west Scotland (Nisbet et al., 1995). However, this trend is not evident for all catchments (Battarbee et al., 1995). This may be due to sulphate reservoirs in the catchment soil and/or the role of nitrogen oxide deposition; consequently, reductions in nitrogen deposition may need to be considered in the near future. Furthermore, the release of nitrate in catchments may be exacerbated by ageing forests reaching nitrogen excess and climate change increasing temperatures and the mineralisation of nitrogen in soils (Stevens et al., 1997b).

At the catchment scale, policy and environmental management has focused upon land-use changes, particularly afforestation. Newson (1996) states that 'the management of the catchment land-use needs to be considered as contributing to a sustainable management of the river catchment in the same way as hard engineering does'. The sites of primary concern are those sensitive areas where acidification resulting from anthropogenic influences could have a detrimental effect upon the aquatic habitats, water quality in the headwater ecosystem and downstream uses. Furthermore, there may also be a legacy of sites where stream acidification may occur as the forestry cycle progresses, and these have yet to be identified.

The Environment Agency and Forest Authority (and their predecessor bodies) have worked in close liaison to drawn up the Forest and Water Guidelines, now in their fourth edition, that highlight the key problems and mitigation measures with respect to afforestation and the aquatic ecosystem. The Forest and Water Guidelines are the prime vehicle for reconciliation of environment protection and afforestation, and are continually updated as the knowledge base expands.

Catchment liming (Comber et al., 1999) and groundwater augmentation (Neal et al., 1997a) have been used in some catchments to provide an 'instant' amelioration of acid stress. However, these are costly, require repeating/maintenance, have no guarantee of success and should not be seen as the sustainable panacea to acidification. Control and prevention at source is the best option.

There is a need to constantly re-assess the management of acidification in an era of rapid change with new concepts and policies arriving in rapid succession, and the mutual interactions of forest and water become complicated by new factors, new locations etc. Consequently, the Environment Agency needs guidance from research literature and its own monitoring networks about the extent and seriousness of present and future forestry impacts on the aquatic impacts (Newson, 1996).

1.2 Headwater ecosystems: An undervalued resource

First and second order streams (i.e. within 2.5 km of their source and mean annual flow less than 0.31 cumecs) represent 94% of all watercourse in Great Britain (Furze et al., 1991; Furze et al., 1993; Furze et al., 1995; and Furze, 1995). However, headwater ecosystems are rarely studied and the dearth of knowledge, in comparison to larger order rivers, makes them a great unknown.

Headwaters make an important contribution to the overall total taxon richness of a river catchment, including the fisheries (Furze et al., 1991, 1993 and 1995; Furze, 1995). Consequently, if the headwaters loose their diversity this is reflected throughout the river catchment. In the same role, the headwaters act as a reservoir/source of recolonisation of the main river downstream after it has suffered a perturbation, such as pollution incidents. Furthermore, the headwaters provide the exclusive habitat for species that are sufficiently rare to warrant national and international conservation status. Large proportions of the upland headwaters have high ecological value and national and international quality designations including National Parks, Sites of Special Scientific Interest etc. Given the significance of headwaters and the current national and international obligations (e.g. Habitats Directive, bio-diversity etc.) the Environment Agency (and other bodies) have a duty to understand and maintain bio-diversity. It is important these habitats are managed and protected to reflect their true value.

While the conservation value of upland headwaters is apparent, they also have high value terms of water resources, fisheries, forestry, agriculture, recreation and tourism that adds a commercial value to the ecosystem and issue of protection and management.

For example, upland headwaters are an important source of both private and public water supply; although they comprise of only 20% of the country's land area they provide about 50% of the water (Robinson et al., 1998). Changes to the volume and quality of the water can be brought about by land-use changes and this can have costly implications to society. For example, if acidification decreases the pH and elevates the aluminium concentrations of raw water it will preclude an affected resource from supply without additional, expensive treatment.

The uplands of Britain also contain the bulk of the nation's plantation forestry. The Kielder forest which, at approximately 600 km^2, is Britain's largest forest and currently produces 400 000 m^3 of timer per year (Robinson et al., 1998) and is commercially important.

In summary, the size and nature of headwater streams means they are particularly sensitive to pollution and changes (e.g. land-use, climate change, acid deposition etc.) and it is necessary to protect this valuable resource and maintain the obligations to national and international legislation. Consequently, good information is required to be able to develop environmental management strategies that balance the conservation and commercial value of these ecosystems in an equitable manner and a risk-benefit framework.

1.3 Research programme: aim and objectives

The overall aim of the Coalburn study is to 'determine in detail the hydrological effects of upland conifer afforestation' (Robinson et al., 1998). The Environment Agency sponsored the water quality element of this research programme to gain information relevant to the monitoring and management of headwater acidification. To this basic aim, the enquiry into runoff processes and pollution climatology have been added. The work presented here is an interface between 'pure' and 'applied' science and the specific objectives include:

1. Assess the episodic acidification status of the Coalburn catchment.
2. Determine the magnitude, duration and frequency of the acid events.
3. Identify the important chemical signatures and variations in the Coalburn rainfall and cloudmist
4. Identify the temporal variations (base-flow, storm-flow and seasonal) in the Coalburn stream water quality.
5. Determine the spatial variability in stream chemistry for the Coalburn catchment.
6. Ascertain if a link can be established between the deposition (rainfall, cloudmist and dry) and stream chemistries.
7. Apply hydrological principles and chemical signatures to conceptualise the likely causal mechanisms underlying the acid events at Coalburn (considering the pollution climatology, flowpaths, residence times and antecedent conditions).
8. Derive a classification system for the acid episodes observed at Coalburn based on the catchment scale response, characteristics and signatures.
9. Apply mixing modelling techniques to the Coalburn data and derive a conceptual Coalburn model of the Coalburn hydrochemical response.
10. Appraise the relevance of the information presented as part of this research programme to public policy and the Environment Agency operations.

1.4 Outline summary

The study presented here uses an extensive database of water quality data gathered through regular sampling, event sampling and continuous monitoring. In summary, the chapters cover the following topics:

Chapter 2	Outlines the physical characteristics of the Coalburn catchment, the previous research at Coalburn and the research framework used in this study.
Chapter 3	Identifies and discusses the important hydrochemical signatures and their variations in time and space; focusing on the rainfall, cloud mist and stream chemistries.
Chapter 4	Utilises the continuous and sampled pH and conductivity data to assess the duration, frequency and magnitude of acid episodes in the Coalburn (briefly considering the biological impact). The continuous data is also examined in terms of its key hydrochemical signatures and use as a diagnostic tool for interpreting the causal mechanisms underlying the acid events.
Chapter 5	A classification system for acid events at Coalburn is derived. A simple conceptual runoff model is then used as the basis of hypothesising the causal mechanisms of nine acid events chosen as being representative of the different classes of event observed in the catchment.
Chapter 6	Mixing modelling techniques are applied to the Coalburn data and the nine events re-examined in light of this. A conceptual mixing model is proposed. The runoff and mixing model are then combined to produce a conceptual Coalburn model.

Chapter 7	The studies reported in the previous chapters are discussed in terms of their relevance to public policy and the Environment Agency operations. A headwater appraisal strategy is discussed and costed to provide a framework for operational investigation of acidification in headwaters.
Chapter 8	Summarises the studies reported in the previous chapters and considers: the contribution to science and policy; potential further work at Coalburn and general future issues.

2 Coalburn: The study catchment

Overview

The uplands of Britain contain the bulk of the nations plantation forestry and the Forestry Authority/Commission and Environment Agency require good quality information to enable sustainable management and planning of forestry activities. This is particularly important in the context of the 1995 Rural White Paper that suggests a doubling of the afforested area in England from 7 to 14 %.

Research on the hydrological and hydrochemical effects of upland afforestation has typically focused upon initial land preparation, mature plantations or harvesting operations, leaving a hiatus in the understanding of the forestry cycle. The Coalburn study offers the opportunity to bridge this gap and is unique in Britain, being a long-term experiment aiming to provide detailed hydrological records of the impacts of afforestation throughout the forestry cycle. The Coalburn catchment was established in 1966 and data has been gathered for five years prior to afforestation and the first 27 years of forest growth.

Since, 1992 the Environment Agency has collected water quality data through regular sampling, event sampling and continuous monitoring, building an extensive database of high resolution water quality data. Data has been collected through the later stages of canopy closure. This stage is likely to represent a period of distinct change in physical, hydrological and chemical terms, as the influence of the forest crop starts to dominate over the residual impacts of ground preparation. This thesis discusses and summarises the water quality at Coalburn and offers a benchmark for future studies to assess the changes in hydrochemistry as the forestry cycle progresses to felling and replanting (2011 and onwards).

2.1 Study catchment

2.1.1 Physical characteristics

Coalburn is a headwater catchment of the River Irthing located 40 km north-east of Carlisle (Figure 2.1, Plate 2.1 and 2.2). The 1.5 km^2 catchment is on the outskirts of Kielder Forest and its topography varies from 330m A.O.D. in the north-west to 270m at the catchment outfall, with a main channel gradient of about 25m km^{-1}. A summary of hydrometric and climatic data are provided in Table 2.1:

Table 2.1 Summary of hydrometric and climatic data for Coalburn

Parameter	Details	Reference/Source
Mean annual precipitation	1350mm - evenly distributed throughout the year and over the catchment.	Robinson et al. (1998)
Snow cover	Average of 31 days per year	Eskdalemuir Met Office Station 1967-96. (30km north)
Penman potential evaporation (grass)	445mm	Robinson et al. (1998)
Canopy interception losses	24-41% 28 %	Hind (1992) Wake (1994) Robinson et al. (1998)
Throughfall	97% of net precipitation	Hind (1992) Wake (1994)
Stemflow	3% of net precipitation	Hind (1992) Wake (1994)
Mean streamflow at the outfall	0.046 cumecs	Robinson et al. (1998)
Maximum recorded discharge	6.00 cumecs	Robinson et al. (1998)
Minimum recorded discharge	Flow may cease during extended periods of dry weather.	Personal observation.

The solid geology of Coalburn comprises of calcareous mudstones, sandstones and shales with some thin limestone bands and coals, belonging to the Upper Border Group of the Lower Carboniferous Period (Robinson et al., 1998; Day, 1970; Frost and Holliday, 1980). The entire catchment is mantled by glacial/fluvioglacial boulder clay derived from the Carboniferous bedrock. The cool wet climate has favoured the growth of a surface layer of blanket/basin peat over much of the catchment. The peat depth varies from zero to greater

Plate 2.1 Coalburn outfall at the weir

Plate 2.2 Coalburn catchment at the automatic weather station

than 5.00m and a maximum recorded depth of 10 m. In broad terms 75% of the catchment is covered by peat bog, the soil type being identified as Long Moss and Winter Hill series, which are thick oligo-fibrous peats, very acid and perennially wet (Clayden and Hollis, 1984). Thinner peat and cambic stagnohumic gley soils (Wilcocks 1 – strongly gleyed clay loam with a humified peat topsoil/surface horizon) cover the remaining steeper slopes (>5%) and are mainly situated in the south east of the catchment (Figures 2.2). The soil/peat distribution creates two distinct sub-catchments. Further soil profile information is given in Hind (1992) and Waterfall (1994), these were analysed from cores taken during excavation of dipwells and piezometer tubes.

2.2 Coalburn history and previous research

The Coalburn study commenced in late 1966 when the land was used for rough grazing for sheep, and vegetation comprised *Molina* grassland, and peat bog species (including *Eriophium*, *Sphagnum*, *Juncus* and *Plantago*). There were some 'sheep drains' dating from the 1940's and 1950's that consisted of shallow ditches about 20m apart; these would have originally been 0.40m deep (MAFF, 1973). These were overgrown and largely inoperative at the start of the study. In early 1967, two parallel boundary ditches were cut to define the catchment watershed and enable the exact area of moorland draining to the weir to be determined, ensuring that it was not cut by the forestry drains.

The original catchment was instrumented in late 1966, and approximately five years of hydrological data collected. In 1972, the Forestry Commission prepared the site by ploughing the entire catchment with a D90 deep double mouldboard plough to cut furrows (open drainage ditches) to 0.80-0.90m depth. The ploughing cut furrows at about 4.50m spacing, generally aligned with the ground slope, and without regular cross drains. The water from the furrows is intercepted by deeper drains or allowed to run directly into the stream. The artificial drainage network at Coalburn increased the natural drainage density by approximately sixty times to 200km km^{-2}.

Figure 2.1 Coalburn catchment

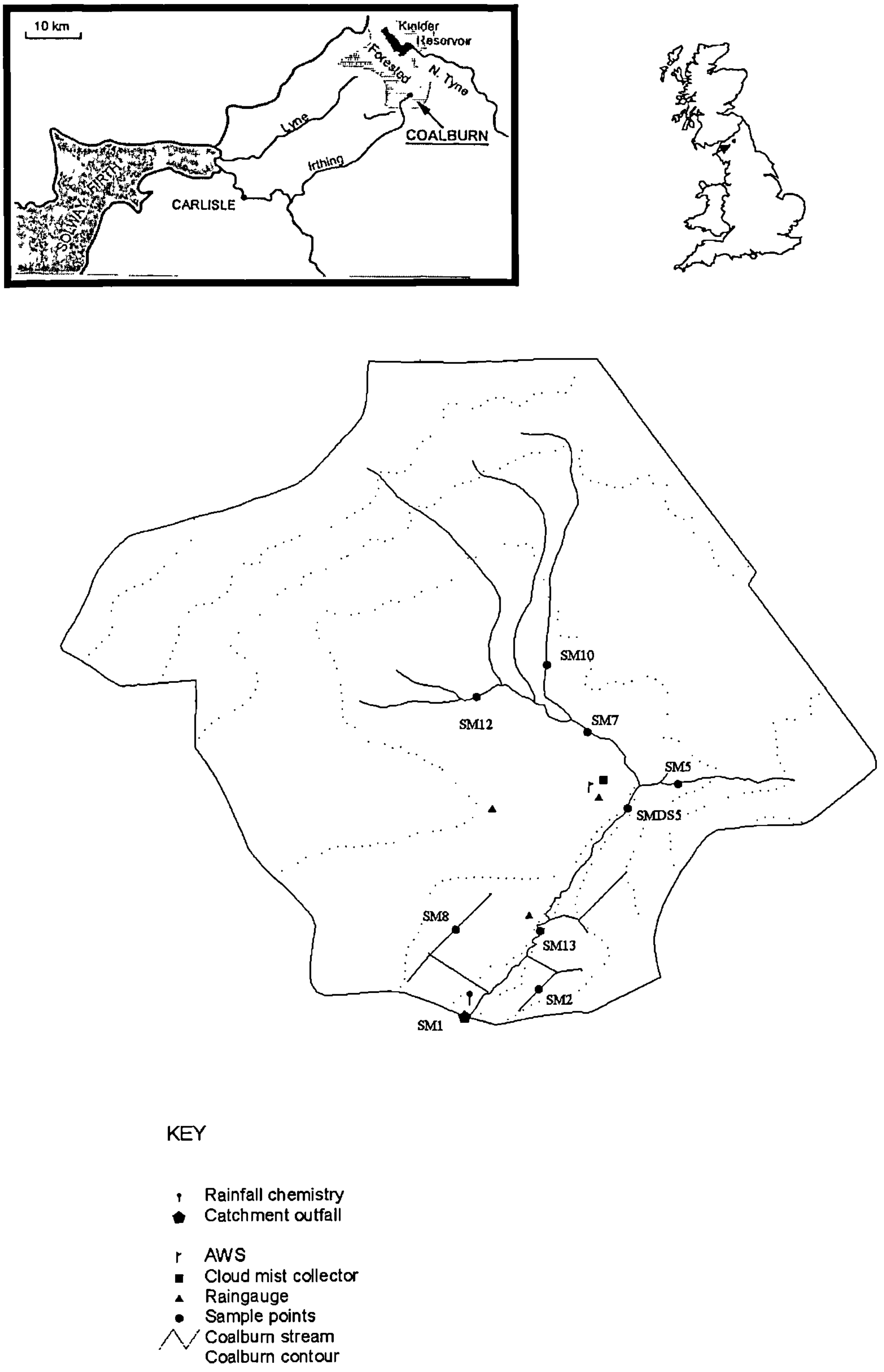
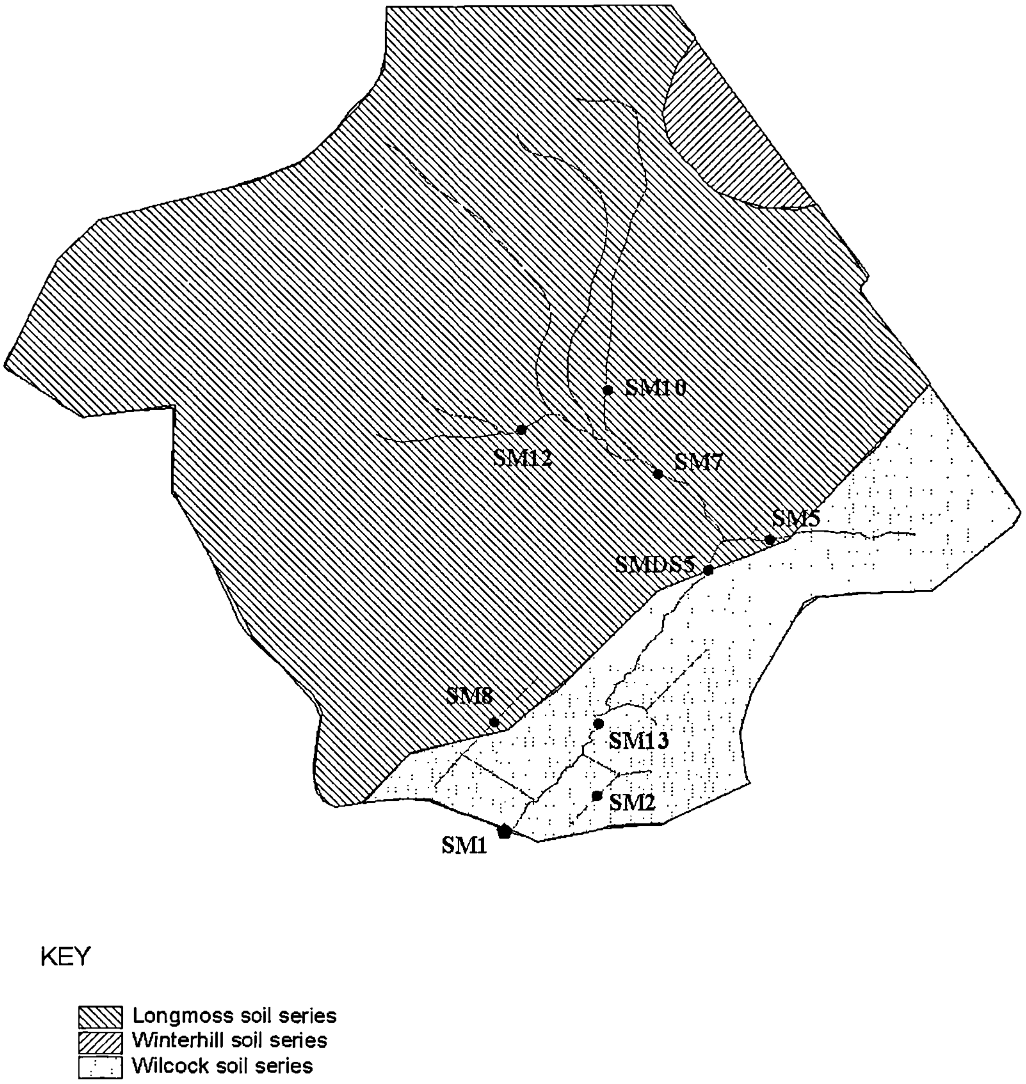


Figure 2.2 Coalburn catchment soils



The excavated material was used to construct turf ridges (as elevated drier sites for planting) and the soil was then left to dry for a year. In spring 1973, the turf ridges were planted with Stika Spruce (*Picea sitchensis*) and some Lodgepole pine (*Pinus contorta*) at about 2m spacing. Severe frost in the lower lying areas of the catchment have left some large unplanted areas; these were not replanted in a deliberate attempt to maintain some habitat for Black Grouse. These unplanted valley floors should not be mistaken as buffer strips as the drains still discharge directly to the channel. Other areas that were left unplanted were around the four raingauge sites (to reduce the effect of tree growth on the raingauge catch) and on the steepest areas adjacent to the main channel, so in total 136 ha or 90% of the catchment was planted.

The site conditions and repeated frosting has meant that while tree growth has been slow it is typical for such an upland site (Table 2.2), with a yield class of 10-12 (i.e. 10-12$m^3ha^{-1}yr^{-1}$ timber growth) (Robinson et al., 1998). On the deeper peat sub-catchment some of the tree growth is in check due to waterlogging and nutrient deficiency.

Table 2.2 Coalburn tree growth

Year	Height (Metres)
5	1.00
12	3.00
19	6.00 to 7.00
23	7.00 to 12.00.

The other important characteristic of the forest crop is the degree of canopy closure and in 1992 around 60% (i.e. 54% of the whole catchment) had reached the stage of canopy closure (Robson et al., 1998). By 1996 the canopy had closed (Robinson, 1998).

In the open areas, the vegetation is still the natural moorland vegetation. However, on the afforested areas the natural and understorey vegetation has been shaded out as canopy closure was achieved and a coniferous 'needle' litter layer is developing.

Table 2.3 Coalburn history

Year	Month	Comment
1966		Geological soil survey of catchment.
	July.	Selection of site for the flow measuring station
	October.	First storage rain-gauges installed
	December.	Flow monitoring weir operational.
1967		Start of first full year of observations. Completion of remaining minor work on the weir in spring.
	May	Standard raingauge network expanded during the year - May (nine gauges) and full network of thirteen gauges completed in September Catchment boundary ditch cut.
1968		Access road to weir and centre of catchment completed; commenced installation of the ground level rainfall gauges.
1969		Decision to delay ploughing until 1972 to extend the calibration period to five years.
1970		Comparison of the ground level and standard gauges.
1971		Two Automatic Weather Stations (AWS) installed in August, producing daily Penman evaporation values.
1972	February	Precipitation network reduced to four sites.
	March	Stream sediment monitoring commenced.
	May.	Rock sulphate applied, and stream concentrations monitored from April to October.
	July-September	Site drained using D90 peat plough.
	November	Boundary drain checked. Break in the flow data from October 1972 until June 1973 when weir repaired and sediment removed.
1973		Trees planted in spring (about 0.20m tall); suspended solids monitoring ended in October Davies, S.H. (1973). 'A study of the variations in water quality of Coalburn caused by the ploughing of the catchment prior to afforestation.' Unpublished dissertation, University of Lancaster, Dept. of Env. Science.
1974		
1975		Largest recorded discharge , peak flow six cumecs.
1976		Catchment boundary checked.
1977		Transfer of catchment to Forestry Commission and North West Water; backup AWS removed, and remaining AWS began to supply hourly meteorological data.
1978		Suspended sediment monitoring; tree heights generally less than one metre.
1979		
1980		Institute of hydrology Report 73 published, summarising the results to date, resulted in renewed interest in catchment study. Robinson, M. (1980). The effect of pre-afforestation drainage on the streamflow and water quality of a small upland catchment. Institute of Hydrology Report No. 73.
1981		Maintenance on weir.
1982		Effects of forestry drainage at Coalburn, described in article in New Scientist.
1983		Reference to Coalburn study in House of Commons debate on upland flooding; tipping bucket raingauge replaced chart recorder in September.
1984		Maintenance work on the weir.
1985		Forest Commission soil survey; repairs to the weir.
1986		Robinson, M. (1986). Changes in catchment runoff following drainage and afforestation. Journal of Hydrology 87. 71-84.
1987		
1988		
1989		Institute of Hydrology rainfall event recorder replaced by National Rivers Authority (NRA).
1990		Telegen logger installed for river level measurement in June; soil measurements on peaty gley side.

Table 2.3 Coalburn history continued

Year	Month	Comment
1991		Temporary weir from May until new weir completed in August.
		Robinson, M. & Hind, P.D. (1991). The Coalburn catchment experiment. North of England Soils Discussions Group Proceedings, 26.
1992		Forest cover survey (mean height 7.00m); catchment boundary walked in November; soil moisture measurement on deep peat side; monthly water chemistry sampling commenced.
		Hind, P.D. (1992) The Coalburn experimental catchment study; An evaluation of process hydrology at canopy closure using solute chemistry. Unpublished report. University of Newcastle Upon Tyne. Department of Geography.
1993	March	NRA AWS records began.
	July	Continuous monitoring of stream pH, conductivity and temperature. Also ultrasonic flow measurement installed to validate high-flow rating.
	November	Biological survey carried out.
		Soil moisture measurements on peat side under closed canopy forest.
1994	February	Water quality sampling started twice monthly.
	March	Howan Burn flow measurement began.
	June	Event autosampler installed at catchment outfall.
		Forest interception study began by Institute of Hydrology.
	July	Cloud mist volume and chemistry monitoring started.
	October	S. Mounsey registered for PhD and took over NRA responsibility for Coalburn catchment.
		Baglee J.A.R. (1994). Shallow groundwater in the afforested Coalburn experimental catchment. Northumberland. Unpublished, MSc thesis, University of Newcastle upon Tyne. Department of Civil Engineering
		Prigg, R.F. (1994). Fish and macroinvertabrate populations of Coalburn, and their interpretations in an acidification context. Technical Memorandum No NB276(2/94). National Rivers Authority North West.
		Robinson, M., Moore, R.E., & Blackie, J.R. (1994). The Coalburn Catchment Experiment - 25 Year Review. R&D Note 270. National Rivers Authority.
		Wake, C. (1994). A study to investigate the influence of a forest canopy, weather regimes and soil type on water quality in the Coalburn catchment. Undergraduate dissertation. University of Newcastle upon Tyne. Department of Geography.
		Waterfall, B.J. (1994). The effect of unafforested riparian zones in a coniferous plantation on stream water quality. Undergraduate dissertation. University of Newcastle upon Tyne. Department of Geography.
1995	June	New pH probe installed.
	August	V notch weirs installed on clay and peat sides of the catchment.
	October	M. Scott took over NRA operational responsibility for Coalburn.
		George, S.A. (1995). The temporal and spatial variability of the water quality in the acidified Coalburn catchment. Undergraduate dissertation. University of Newcastle upon Tyne. Department of Geography.
		Grundy, C.D. (1995) The influences of hydrological pathways on runoff chemistry at Coalburn. Undergraduate dissertation. University of Newcastle upon Tyne. Department of Geography.
		Hughes, L.F. (1995). An investigation of rainfall and runoff chemistry at Coalburn. Undergraduate dissertation. University of Newcastle upon Tyne. Department of Geography.
		Mounsey, S.C. & Newson, M.D. (1995) Acid episodes in the Coalburn catchment. Proceedings of the British Hydrological Society 5th National Hydrology Symposium p5.17-5.27. Presented 6 September 1995.
1996	April	S. Jones took over Environment Agency operational responsibility for Coalburn catchment.
	November	Spatial sampling started.
		Cloud deposition installed above the forest canopy.
		Forest health plots installed by the Forestry Commission.
		Butcher, D.P., Labaz, J.C., McNish, J.H. & Shacklock, J. (1996). Relative sensitivity to acidification of the Kielder Region, Northumbria.
1997	January	H. Waugh took over the Environment Agency operational responsibility for the Coalburn catchment.
		Ultrasonic flow measurement equipment removed
		Gauging section and bridge installed upstream.
		Flow measurement started on four forest drains.
		First measurement of forest transpiration.
	May	Spatial surveys started by Newcastle University.
	September	Telemetry TBR installed
		Forestry Commission peat depth and soil survey carried out.

The hydraulic efficiency of the smaller drainage furrows has decreased overtime due to soil infill, vegetation colonisation and peat shrinkage. In contrast, some of the larger drains would appear to be actively eroding downwards and in some places have cut through the peat layer and are into the underlying mineral boulder clay material.

A summary of the major activities, milestones, and research (published and unpublished) for the Coalburn catchment are listed in Table 2.3. This provides a substantial foundation upon which this element of the Coalburn research programme has been built.

2.3 Instrumentation and analysis: hydrology

Data for this thesis has been collected by the Environment Agency and Newcastle University during the period 01 September 1993 to 31 December 1997. This followed the refurbishment of the Coalburn catchment instrumentation by the then National Rivers Authority (see Robinson et al., 1994). This section outlines the instrumentation and analysis used.

The Coalburn research effort is a partnership and data from the other organisations (Institute of Hydrology (IoH); Forestry Commission (FC) and North West Water Ltd (NWW)) has been utilised. Where used this is clearly acknowledged and where applicable a brief methodology and reference has been included in this section.

2.3.1 Precipitation

Precipitation was measured using a network of three standard and ground level storage rain gauges sited across the catchment (Figure 2.1), these were read twice monthly. Wind turbulence around standard level gauges generally causes them to undercatch compared to the true catch of ground level gauges in upland environment. Robinson et al. (1998) calculated an average undercatch of five percent for standard gauges at Coalburn.

The rainfall was distributed temporally (hourly) using a 0.2 mm tipping bucket raingauge (TBR) at the automatic weather station (Figure 2.1). There was a second TBR at the catchment outfall; however, this is outside the catchment and while useful for validation and backup purposes it was not used in the calculation of the water balance. The rainfall areal average was calculated using the following Theisen weightings derived by Dr M. Robinson (IoH): Site 1 = 0.1262; Site 5 =0.4385; and Site 11 = 0.4352.

The raingauges and TBR are operated and maintained by the Environment Agency and receive regular inspections, replacement and calibrations to ensure the data are accurate. The data are stored on the Environment Agency archives and has been validated by near neighbour comparisons and by the Meteorological Office (Robinson et al., 1998).

The daily rainfall values from the AWS tipping bucket raingauge were used to calculate the antecedent precipitation index (API) as per Shaw (1988):

$$\mathrm{API}_t = \mathrm{k} \, . \, \mathrm{API}_{t-1}$$

where API_t is the index *t* days after the first day's API_0. The value k reflects the potential loss of moisture and varies between 0.85 and 0.98 (Shaw, 1988). In this case, a k value of 0.915 was used; the absolute value of k is not critical as the API values are only used for comparative purposes. At the beginning an arbitrary value of API_0 can be assumed, in this case zero, as its effects soon disappear after 20 days or so (Shaw, 1998).

2.3.2 Cloud mist

Cloud mist is deposition of mist or cloud on to the vegetation. This water may enter the catchment system or become re-evaporated. There is no record of cloud levels at Coalburn but Fowler et al. (1989) suggested that in upland ecosystems cloud mist may be an important contributor to the wet deposition component of chemical inputs. The importance of the cloud mist component can be increased if a catchment is forested as the canopy is taller and aerodynamically rougher than shorter moorland vegetation (Wilkinson et al., 1997)

Volumetric assessment of cloud mist were collected at the AWS site by the Forestry Commission from July 1994 using the standard passive cloud collector gauge developed by the Institute of Terrestrial Ecology (Milne et al., 1988) to simulate cloud mist deposition. The cloud mist condenses on nylon filaments, drains to a funnel and the volume is recorded by a tipping bucket recorder. The instrument is capped with a 1.2m lid to exclude rainfall droplets larger than 0.5mm diameter entering the collector when windspeeds are less than 5 ms^{-1}.

Nevertheless, some rainwater contamination can occur under windy conditions, but the collector provides a good estimate of the cloud water volumes. The cloud mist results are discussed in Robinson et al. (1998), the main conclusions for the Coalburn catchment were:

- *Calculated cloud water content averaged 0.2 gm*$^{-3}$.
- *Cloud deposition occurred for 6% of the time, approximately 500 hours per annum. This includes periods where the windspeed was greater than 5 ms*$^{-1}$*, and the duration may, therefore, be an overestimate.*
- *Annually estimated cloud mist contribution to the water balance is 50-90mm.*
- *The small contribution of cloud deposition is supported by the absence of any flows from the IoH interception sheets when there was no rainfall (i.e. any deposition during periods of low cloud, but no rainfall, did not exceed the forest storage capacity of about 0.8mm).*

There is a degree of uncertainty in analysing cloud mist results as during periods of high wind (>5 ms^{-1}) as rain can be driven onto the filaments causing the gauge to over-read, while on dry windy days any cloud mist condensing on the filaments may be re-evaporated before reaching the storage container. It is difficult to assess how representative the cloud mist sampler volumes are compared to that deposited on the forest crop and its contribution to the water balance.

2.3.3 Meteorological variables

The following meteorological variables were recorded on an hourly basis by an Automatic Weather Station (AWS) (Figure 2.1):

Dry and wet bulb temperature	(Degrees Celsius)
Net and solar radiation	(mWm^{-2})
Relative humidity	(Percentage)
Wind speed and direction	(ms^{-1} and degrees)

The AWS was downloaded monthly and the data validated in by the Environment Agency and subsequently by IoH. Eskdalemuir is the nearest Meteorological Office site that can be used for comparisons, data validation and infilling. The only non-routine maintenance that has been necessary during the study period was the replacement of the wind direction sensor in February 1997. Data prior to February was compared with results from the IoH above canopy AWS and there was no indication that the Environment Agency data was erroneous.

It should be remembered that while the AWS gives a good indication of the local/micro scale weather conditions the mesoscale weather patterns are also important with regard to catchment conditioning (Newson, 1986).

2.3.4 Forest canopy

The Institute of Hydrology installed two net rainfall sheets under the forest canopy in the Coalburn catchment (Robinson et al., 1998), these were, initially, under a 7.00m and 9.00m stand. Each instrument consisted of a large plastic sheet collecting both throughfall and stemflow from a known area, directing the collected rain to 1 litre TBR's. The TBR logged each tip on a counter and these were read at regular intervals by the Environment Agency and Forestry Commission, also for a period they were connected to a logger to distribute the net rainfall temporally. The results are presented in Robinson et al. (1998).

Newcastle University studies have made simpler measurements of the throughfall and stemflow quantities at Coalburn; these were made at two plots on each sub-catchment type, methodologies and results for these studies can be found in Hind (1992) and Wake (1994).

2.3.5 Soil moisture and saturation

Since January 1983, water levels have been measured in a transect of seven dipwells installed at right angles to a plough furrow in an area of deep peat to the west of the weir. Throughout the study the depth of water in each dipwell was recorded at least twice monthly during the surveys carried out by the Environment Agency and Forestry Commission. Newcastle University have operated a further two dipwell transects under the canopy on both the peat-gley and peat soils (Hind, 1992; Waterfall, 1994).

Since spring 1992 Newcastle University have made regular (approximately monthly) soil water content measurements using a ‘Wallingford’ neutron probe. Measurements were made over the soil profile depth to over one metre at which point there was no change in the soil water content. Three sites were chosen for to represent the different soil and vegetation combinations. Robinson et al (1998) summaries the results as follows:

- *Peaty gley site is drier than the two peat sites.*
- *Peat soils are drier under the forest.*
- *Seasonal range of water content for two peat soil sites is greater under the closed canopy forest than under grass, implying a greater total use by the forest.*
- *There is a weak trend over time suggesting that with growth of the trees the forest soils are becoming progressively drier.*

Between October 1990 and November 1993 soil water potentials were recorded on a 30 minute basis at the same three sites used for the neutron probe access, Robinson et al. (1998) summarised the results:

- *There is a rapid response of soil water to rainfall, especially in the upper peat layers. Once this reaches the extensive network of plough drains it can be transmitted quickly to the catchment outlet. No point in the catchment is more than 2.5m away from one of these channels.*

- *For mid drain spacing for the peat site under grass the water table was within 0.5m of the ground surface throughout the year. In contrast, unsaturated conditions persisted at that depth under the forest for about 20% (peat soil) and 25% (peaty-gley). At a depth of 0.2m the unplanted grassland was saturated for >50% of the time while the forested peat and peaty-gley were saturated 5% and 10% respectively.*

In July 1993 two transects of piezometers were installed, one on the peaty-gley area of the catchment, comprising eight sample sites and nineteen piezometer tubes. The peat transect had six sites and six piezometers. Results from these are presented in Waterfall (1994) and the sites have continued to be read on an approximately monthly basis. These were subsequently supplemented by Baglee (1994).

2.3.6 Streamflow tributaries and drainage ditches

The soil and peat distribution creates two sub catchments that are likely to have different hydrological signatures (Figure 2.2). To assess if the hydrological response of the drainage ditches were different two V notch weirs were installed at SM2 (peaty-gley sub catchment) and SM8 (peat sub-catchment) on 19 October 1995 (Figure 2.1). These sites had previously been used by studies carried out by Newcastle University. Stage was recorded every fifteen minutes using a pressure transducer; data was downloaded, validated and archived by the Environment Agency. It was then possible to derive flow using the standard equations for a V notch weir.

2.3.7 Streamflow catchment outfall

Streamflow from the catchment was recorded on a fifteen-minute basis using a compound V notch and broad crested weir (Figure 2.1); a full description can be seen in Robinson et al. (1994). The weir was designed so the catchment flow was in the notch for 98 percent of the time, which allowed the maximum accuracy and sensitivity. Stage was logged on a fifteen-minute basis using a logger and downloaded daily by remote telemetry. A chart recorder was used to back up and validate the logger data. The Environment Agency is responsible for validating and archiving data.

Stage was converted to flow using the following rating that had two segments:

Segment 1 $\text{Stage} \leq 0.63\text{m} \ \text{Flow} = 1.3688(\text{Stage}+0.001)^{2.5041}$

Segment 2 $\text{Stage} \geq 0.63\text{m} \ \text{Flow} = 8.1520(\text{Stage}-0.463)^{1.6363}$

The rating equations were validated by check gauging and volumetric measurements, generally monthly. The ratings equations were reviewed every six months by the Environment Agency. Recently a bridge has been built upstream of the weir to enable high-flow gauging to validate the upper segment of the rating. Initial results have indicated that Segment 2 may be underestimating the flow, although more gauging is required to confirm this. In summary, there is an accurate and complete stage/flow times series with only a few isolated occasions where data are missing.

Elementary hydrograph separation was carried out for the events studies in Chapter 5. The hydrograph was separated from a point on the rising limb where the flow began to rise to the point on the recession curve where the logarithmic plot of flow became linear (Ward and Robinson, 1990). The two points were joined and the flow above this line was attributed to storm-flow (Q_s) and the flow below attributed to base-flow (Q_b)

2.4 Instrumentation and analysis: hydrochemistry

2.4.1 Sampling protocol

The Environment Agency samples were collected according to the environmental sampling quality management system (Environment Agency Manual). The important elements of sampling process were to rinse the bottles before filling (to avoid getting solids in the bottle), to avoid skin contact with the inner surfaces of the bottles and lids and to leave no air gap in the bottle. Samples were stored in a dark cool place ($< 4^{oC}$) and were, generally, transported to the laboratory on the same day.

2.4.2 Environment Agency laboratory procedures

A small number of the initial samples were analysed at the Carlisle laboratory. However, after October 1993 the analysis was carried out at the Environment Agency National Laboratory Service at Nottingham. The determinands and standard methodologies used to analyse the Coalburn samples are described in Table 2.4. A reference for a detailed methodology is included.

In some instances, particularly the rainfall and cloud mist samples, the lack of sufficient volume meant a full analysis for all determinands could not be carried out; the analysis was then done on a prioritised basis.

The Coalburn samples required low level analysis compared to the normal water samples analysed by the laboratory. Throughout the study, there was a problem with the Coalburn samples not receiving this low-level analysis and the results were reported as 'less than' values. Where sample results have been reported as 'less than' values, for whatever reason, the results have been omitted from the study.

Table 2.4 Laboratory analysis methods

Determinand	Units	Methodology	MRV	Reference
pH	Unitless	pH meter	n/a	ISBN 0117514284
Conductivity at 25^{oC}	µScm^{-1}	Conductivity meter.	10	ISBN 0117514184
Colour	mgl^{-1}	Colorimetry	1	ISBN 0117519553
Ammonia as N	mgl^{-1} as N	Colorimetry (c)	0.03	WRc TR 119
Nitrogen Oxidised Total	mgl^{-1} as N	Colorimetry (c)	0.2	ISBN 0117515930
Nitrate as N	mgl^{-1} as N	Calculated det	0.2	Calculated det
Nitrite as N	mgl^{-1} as N	Colorimetry (c)	0.0004	ISBN 0117515930
Orthophosphate	mgl^{-1}	Colorimetry (c)	0.02	ISBN 0117515825
LL Nitrogen Oxidised Total	µgl^{-1} as N	Colorimetry (b)	3	As above.
LL Nitrate as N	µgl^{-1} as N	Calculated det.	3	Calculated det
LL Nitrite as N	µgl^{-1} as N	Colorimetry (c)	0.5	ISBN 0117515930
LL Ammonia as N	µgl^{-1} as N	Colorimetry (b)	3	As above.
LL Orthophosphate	µgl^{-1}	Colorimetry (b)	1	As above.
Alkalinity pH4.5	mgl^{-1} as $CaCO_3$	Gran Alkalinity	0.47	ISBN 0117516015
Chloride	mgl^{-1}	Colorimetry	0.50	ISBN 0117516260
Silicate	mgl^{-1} as SiO_2	Colorimetry	0.2	ISBN 01175115574
Sulphate	mgl^{-1}	ICPOES	0.50	ISBN 0117522406
Sodium	mgl^{-1}	ICPOES	0.40	ISBN 0117522406
Potassium	mgl^{-1}	ICPOES	0.04	ISBN 0117522406
Magnesium	mgl^{-1}	ICPOES	0.06	ISBN 0117522406
Calcium	mgl^{-1}	ICPOES	0.20	ISBN 0117522406
TOC	mgl^{-1}	(a)	0.5	Dorhrmann DC80
DOC	mgl^{-1}	(b)	0.5	Op. Manual
Aluminium	µgl^{-1} as Al	ICPOES	10	ISBN 0117522406
Manganese	µgl^{-1} as Mn	ICPOES	30	ISBN 0117522406
Iron	µgl^{-1} as Fe	ICPOES	10	ISBN 0117522406

Key

LL	Low Level.
MRV	Minimum recorded value
ICPOES	Inductively Coupled Plasma Optical Emission Spectroscopy.
(a)	UV Persulphate and IR detection.
(b)	SKALAR – Air segmented continuous flow analyser.
(c)	Flow injection analysis (FIA) and discrete analyser.

Nitrogen can exist in several different forms and the water industry tends to express the concentrations of these compounds as the elements, i.e. the laboratory provided the nitrate, nitrite and total ammonia expressed as mgl^{-1} of N, this is converted to mgl^{-1} as follows:

Total Ammonia (mg/l) = (Molecular weight/Nitrogen atomic weight) . NH_4asN
= 18/14 . NH_4 as N
Nitrate (mg/l) = 62/14 . NO_3 as N
Nitrite (mg/l) = 46/14 . NO_2 as N

2.4.3 Newcastle University laboratory procedures

The parameters measured for this study at Newcastle University laboratory were pH, conductivity and alkalinity. The pH and conductivity were measured as per methods in Allen (1989). Alkalinity determinations were carried out using two different methods discussed below.

2.4.4 Alkalinity measurements at Coalburn

For routine estimates of low alkalinity waters, such as Coalburn, the Gran procedure (after Gran, 1952) is recommended to minimise errors. Two methodologies were utilised for determining Gran alkalinity in the study, the first from the Environment Agency and, the second, from the Institute of Hydrology.

For low alkalinity natural waters (< 20 mg/l as $CaCO_3$), the Environment Agency laboratory used a Gran plot method. Using an acid titration procedure, the sample was titrated to pH 4.5 (±0.05) and the titre recorded; the titration was then continued to pH 4.2 and the titre recorded. In the pH range 4.2 and 4.5 it is assumed the plot of hydrogen ion concentration against volume of standard acid becomes linear, and this line is extrapolated back to the zero hydrogen ion concentration and the intercept is defined as the true equivalence point due to the total alkalinity. The precise methodology is detailed in ISBN 0117516015.

The Institute of Hydrology Method (Colin Neal pers comm.) uses a two stage alkalinity measurement based on acidimetric Gran procedures, made in two pH ranges:

Alk_{Gran1}	**pH 4.5 to 4.0** Bicarbonate and hydroxyl ions have fallen to insignificant concentrations, and all inorganic aluminium species in solution (except those which are fluoride bound) are reduced to Al^{3+} form.
Alk_{Gran2}	**pH 4.0 to 3.0** Organic alkalinity is included.

This approach is consistent with the type of buffering processes expected in acidified waters. The method involves titrating the solution to a pH of 4.00 and 3.00 respectively, noting the volume of titrant used. The true equivalence point is given by the intercept of a line fitted through the linear segment of the titration curve.

The alkalinity measurements determined by Newcastle University used both of the above procedures, noting the titre added at pH 4.5, 4.2, 4.0 and 3.0. This allowed the alkalinity to be calculated using the Environment Agency and Institute of Hydrology methodologies and also comparison of the results. This was particularly useful as the Environment Agency laboratory could not adopt the Institute of Hydrology methodology, and the comparison of results gave an indication of the performance and limitations of the Environment Agency method. A detailed comparison of the different methodologies is presented in Chapter 6.

2.4.5 Bulk deposition

Bulk deposition was collected near the catchment outfall (Figure 2.1), the collector was an adapted monthly raingauge with a plastic funnel and storage bottle and spikes on the rim to minimise avian contamination.

From 02 March 92 samples were collected monthly up to 01 January 1994, after which sampling was carried out twice monthly, in tandem with the raingauge reading. This allowed the calculation of an areal average rainfall input during each deposition period and the bulk deposition load. The ground level gauges were used to calculate the bulk deposition load as they better represented the true catchment input.

2.4.6 Cloud mist

Cloud mist samples were collected from July 1994 using a second cloud mist collector as described in section 2.32. In this case the cloud mist condenses on the filaments, drains to the funnel and a plastic container. Samples were collected twice monthly in tandem with the raingauge reading. The low volume of the sample was problematic and analysis for all determinands could not always be carried out.

2.4.7 Forest canopy

During rainfall events that coincided with the Environment Agency spatial sampling a sample of the net rainfall from the IoH interception plots was taken by catching the contents of the tipping buckets. Further results are available in Hind (1992), Wake (1994) and George (1995) who collected throughfall and stemflow samples.

2.4.8 Soil water

Previous studies have sampled soil water quality and the methods can be found in Hind (1992), Waterfall (1994), Baglee (1994) and George (1995), sampling the network of soil pits, dipwells and piezometers in the Coalburn catchment.

2.4.9 Tributaries and drainage ditches

Sampling of the tributaries and drains was carried out to assess the spatial variability in the stream chemistry (Figure 2.1). These sampling points had been used by Hind (1992) and enabled comparison of the contemporary and historical data. The primary aim of these surveys was to identify the high and low flow chemical signatures in the catchment, particularly alkalinity. The Environment Agency surveys analysed the samples for the determinands listed in Table 2.4, while the Newcastle University surveys of the catchment were analysed for pH, alkalinity and conductivity.

2.4.10 Main river at outfall: routine and event sampling

Coalburn water was sampled routinely, at least twice monthly, at the gravel trap upstream of the weir and analysed for the determinands in Table 2.4. Alongside these samples a second sample was taken for NWW; these samples were analysed for pH, conductivity and haloform precursors. However, the NWW samples were analysed for conductivity at 20^{oC}; this means the results are not directly comparable to the Environment Agency samples or continuous data, that were corrected to 25^{oC}. To resolve this problem the following correction was applied to the NWW data:

Specific Conductivity (25^{oC}) = 1.112 . (Conductivity 20^{oC})

This correction may introduce a small error into the NWW data if the corrected data were compared to the actual measurement at 25^{oC}, for example a samples on 04 June 1994 were analysed for conductivity at 20^{oC} and 25^{oC}:

Conductivity at 20^{oC}	= 110 μScm^{-1}
Conductivity at 25^{oC}	= 129 μScm^{-1}
Corrected conductivity at 25^{oC}	= 110 * 1.112 = 122 μScm^{-1}.

In this instance, the difference is 5%, acceptable given that analysis and within sample variations may be greater. The NWW conductivity data have been included with this correction.

Routine sampling was augmented by sampling storm events using a Rock and Taylor auto-sampler triggered by stage. The stage threshold was varied according to base-flow and the frequency of sampling during the event varied between fifteen and sixty minutes. Hourly sampling was necessary to capture both the rapid initial changes in chemistry and the entire event due to the slow recovery at Coalburn. The main failing of the event sampling strategy using a stage threshold trigger was the omission of sampling below the trigger threshold. Consequently, critical changes in the streamflow chemistry during the very early phases are missed, and this may be the focus of future work.

A further problem with the auto-sampler was one of sample decay. The auto-sampler samples had the capacity to sample for up to 48 hours with an hourly sampling frequency; this meant the initial samples could have decayed, since during this time the samples were open which could lead to degassing (changing the pH and/or conductivity) and/or contamination.

2.5 Continuous water quality data

Research has focused on the hydrochemical processes that produce acid events; however, it is also important to determine the magnitude, duration and frequency of the events. Many studies have done this by sampling river water quality using sampling strategies as detailed in section 2.4 and then applying statistical techniques to estimate the characteristics of the water chemistry during extreme events.

There are few catchment studies in the UK that benefit from long-term continuous data for acid events. Good quality continuous data are valuable as the extreme values are observed rather than estimated, using questionable statistical techniques (Robson, 1993). Hence, continuous data allows a more detailed calibration of the water quality variation and elucidates the risks/errors in carrying out a 'normal' sampling programme.

The time resolution quality of continuous data far exceeds even the most intense sampling regime; however, without good maintenance submerged electrodes can generate poor quality continuous data (Robson, 1993). Ideally continuous field monitoring of would be as accurate and sensitive as laboratory equipment, however, field monitoring has to trade some sophistication for practicality to operate under harsh conditions, making continuous measurement problematic at the best of times. Despite this, continuous monitoring will generate large volumes of data that are ideally suited to storage and analysis on computers. Once the data are archived, extreme care must be exercised when quoting figures; deriving trends/statistics; or comparing data between different streams or between widely spaced time periods; as the data may include errors, even when corrected (Robson, 1993).

2.5.1 Continuous pH measurement at Coalburn.

From September 1993 to date, Coalburn pH was continuously measured in the weir stilling pool at the catchment outfall. To be precise continuous pH (pH_c) data consist of discrete fifteen-minute samples; however, it is referred to as continuous. A Fisher-Rosemount Model 381 pH combination electrode (specifically designed for low ionic strength waters) was used. The combination electrode had a double junction KCl gel filled reference cell, a glass measuring electrode with a KYNAR3/Ceramic liquid junction. The electrode had a pH measurement range of 0 to 14 and automatic temperature compensation between 0 and 100^{oC}. The pH electrode was connected to a Rosemount analyser and TG1150 logger. The data was downloaded remotely on a daily basis.

The electrode was regularly replaced as per manufacturers recommendations and two Fisher-Rosemount Model 381 pH electrodes were used during the study period, as follows:

Electrode 1:	September 1993	to	31 May 1995.
Electrode 2:	01 June 1995	to	31 December 1997.

Routine calibrations were carried out by Newcastle University, at least monthly, using 4, 7 and 10 standards (BDH solutions). The electrodes have performed well with little drifting (Stelling, Pers. Comm.). The differences between the sampled and continuous values show a consistent relationship, which suggests the calibration and replacement strategy minimised any significant drifting errors (Figure 2.3).

The electrode was routinely inspected for fouling by staff visiting the catchment and the necessary remedial action was taken. Daily examination of the data during downloading was useful in the early identification of problems.

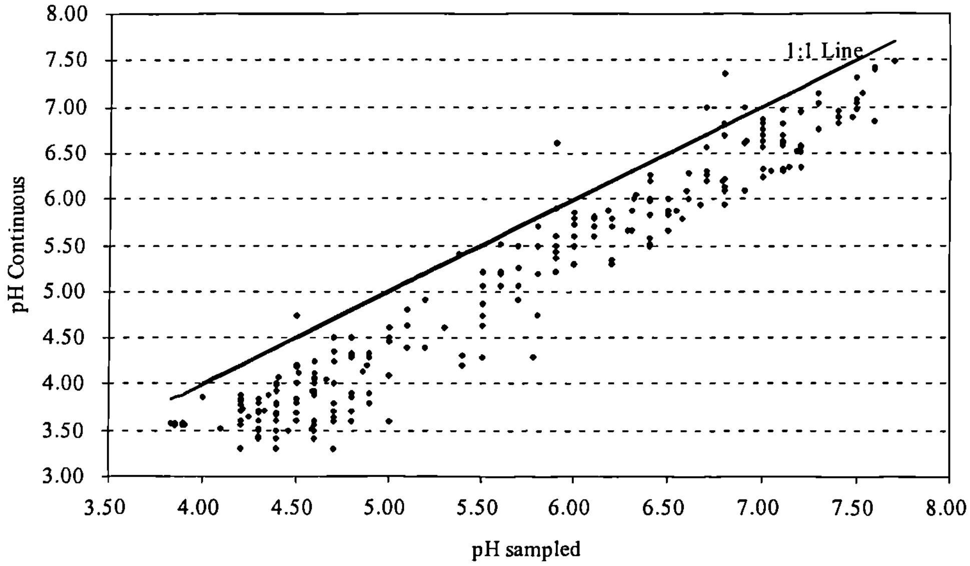
Even with an intensive maintenance regime operating the continuous pH electrodes in such a remote/harsh catchment was problematic. One of the problems has been maintaining the battery power supply that are trickle charged by a wind generator and solar panels; on occasions the lack of charge has resulted in power failure. In contrast, the voltage regulator has been damaged by power surges. Other problems include interference from military aircraft (MoD ranges nearby), mobile phones and cables being nibbled by wildlife:

consequently, the data set has data gaps; the raw data are stored on the Environment Agency archives.

2.5.1.1 Comparison of pH sampled and pH continuous

pH measurement at Coalburn outfall was carried out at two points. The continuous electrode and auto-sampler *measured* pH in the weir stilling pool, due to their infrastructure requirements. Routine samples were taken approximately 30m upstream at the gravel trap. The two sampling points have different physical characteristics, the routine samples being from the natural channel and therefore likely to be representative of the true catchment output. In contrast, the continuous pH and auto-sampler measurements were from the weir pool: a relatively large deep body of still water in a concrete channel, with a layer of sediment at the bottom. Stagnation of water during low flow conditions may allow interactions with the sediment and concrete that could influence pH values, most probably increasing them. Furthermore, stratification and diurnal variations of the pool have been observed under base-flow conditions. Therefore, measuring the pH at one point in the weir pool may be unrepresentative of the water body, which in turn could be uncharacteristic of the catchment.

Figure 2.3 Sampled and continuous pH measurements



The likely causes of errors in the pH_c measurement at Coalburn include:

1. Measurement of pH in low ionic strength waters, such as Coalburn, is problematic due to an insufficient flux of ions to the electrode. This introduces a negative bias to the pH measurements resulting from the junction potential (Davison and Woof, 1985; Davison and Gardner, 1986). This error is likely to be larger in field measurements as the combination electrode does not perform as well as the higher quality laboratory equipment. A plot of pH_c against pH_s clearly demonstrates negative bias (Figure 2.3).

2. The continuous electrode at Coalburn can be subject to a turbulent stream flow during storm events, that may produce a stirring shift. Under laboratory conditions these can be of the order 0.1-0.2 pH units (Davison, 1987). In contrast, pH_s is measured under quiescent conditions.

3. pH_c field measurements are made under harsh conditions with low ionic strength stream water, rapidly changing pH and a turbulent medium. Under such conditions the electrode becomes less sensitive and errors can be introduced due to increased response time and noise. Furthermore, during winter the electrode is exposed to storm damage and freezing conditions (that may be below the temperature compensation); whilst during the summer months heating and low flow can cause problems such as algal growth on the electrode. In contrast, laboratory measurements are made under *ideal* conditions and data are likely to be more accurate.

4. Discrepancies between field and laboratory measured pH may be introduced due to changes in the carbon dioxide equilibrium. Considering this effect on each of the sampling strategies:

    - Routine river samples bottles are *filled to the brim with no air space and* sealed. This minimises any changes in the carbon dioxide equilibria between sampling and pH measurement in the laboratory. The samples are **not** stirred to minimise the carbon dioxide degassing.

- Event samples are stored for a period in the auto sampler where the bottles are open which allow the samples to equilibrate with the atmosphere by the time they are analysed.

- The continuous electrode measures Coalburn pH_c instantaneously during events and the stream may not be equilibrated.

As a result the laboratory measured pH values, although subject to ±0.05 error, are likely to be most representative of the pH of Coalburn, whilst continuous field measurements (pH_c) involve a greater degree of uncertainty. The difference between pH_s and pH_c ranges from 0.29 to -1.40 with the largest values tending to occur at the lowest pH values, coincidentally the range of most interest.

Despite errors in pH_c measurement at Coalburn the typical trace is smooth (Chapter 4 and 5). This suggests the errors are highly auto-correlated, meaning that if a reading underestimates the true state it will tend to be followed by a series of readings with a similar error (Robson, 1993). This implies that over the short to medium term the data may be systematically biased. If the errors were independent, the data would display a 'noisier' trace.

To improve the validity of pH_c a correction can be derived from pH_s data, which takes into account the overall bias of the continuous electrode, flow conditions, and stream chemistry. However, it is difficult to derive a correction that fully compensates for the complex processes causing the observed error in pH_c, as the relationships are not uniform over the pH range (for example pH error and flow).

Linear regression was used to derive corrections for the raw pH_c using the pH_s data. Tables 2.5 and 2.6 list the time periods and co-efficients for the best corrections derived for each electrode based on an equation with the following form:

$pH_{corrected}$ = $A + B \cdot pH_c + C \cdot Time$
$pH_{corrected}$ = Corrected continuous pH data.
pH_c = Raw continuous pH data.
Time = Time in days from start of period
A, B and C are constants.

Table 2.5 Correction for pH electrode 1

Start Date	Finish Date	A	B	C	R^2 (%)	S	N
18-Sep-93	31-Dec-94	1.43	0.841	0.000118	96.4	0.2032	65
01-Jan-95	31-May-95	1.57	0.777	0.000042	95.6	0.1943	53

Table 2.6 Correction for pH electrode 2

Start Date	Finish Date	A	B	R^2 (%)	S	N
01-Jun-95	07-Jul-95	1.164	0.894	94.0	0.2012	24
08-Jul-95	05-Jul-96	0.710	0.940	97.4	0.1804	47
06-Jul-96	31-Dec-97	0.537	1.003	96.9	0.2279	64

Note - a time term has not been included for Electrode 2 as it did not improve the corrections significantly.

Derivation of a correction is complex and is not the panacea of data quality problems encountered with continuous pH electrodes. For Coalburn the corrections improve the data validity; however, errors of up to ± 0.67 and an average of ±0.2 pH units still exist in the corrected pH_c data compared to pH_s. The discussions have also highlighted that a correction formula derived for a specific period of time is rarely applicable for the same stream and/or electrode at another point in time.

In conclusion, sampled pH data are likely to be most representative of Coalburn stream pH, despite sample decay, and should be used as the **primary** source of numerical pH data.

2.5.2 Continuous conductivity measurement at Coalburn

From September 1993 to date Coalburn conductivity was measured continuously at the catchment outfall in the weir stilling pool. A Rosemount Analytical Model 150 conductivity electrode was used, with the data processed by a Rosemount analyser and logged every fifteen minutes. The Rosemount sensor was capable of measuring conductivity between 0 and 20000 μScm^{-1} and had automatic temperature correction to 25^{oC} between 10^{oC} and 121^{oC}.

A single electrode was used to measure conductivity throughout the study period. Routine calibrations were carried out by Newcastle University, at least monthly, using an 84 μS/cm standard, this reflected the low conductivity of the waters being measured. The electrode performed well, with a slight bias towards negative drifting between calibrations, this was of the order of 5 μScm^{-1} at the maximum (Stelling Pers Comm). There were no problems with regard to damage, drifting, poor calibration etc. to suggest that replacement of the electrode was necessary.

The electrode was routinely inspected for fouling by staff visiting the catchment and the necessary remedial action was taken or the problem reported. Daily examination of the data, as it was down-loaded, was useful in the early identification of problems. However, even with an intensive maintenance regime operating the conductivity electrode in such a remote/harsh catchment has been problematic (see above). Consequently, the data set has some data gaps, a full set of the raw data are stored on the Environment Agency archive.

2.5.2.1 Comparison of conductivity sampled and conductivity continuous

The errors that are likely to affect the Coalburn continuous conductivity measurements include:

1. Coalburn waters typically have a conductivity of 34 - 205 μScm^{-1}, which is at the lower end of the operating window for the electrode and errors increase significantly as conductivity decreases (Rosemount Analytical Model 150 operation manual). Furthermore, at low conductivity the samples are more susceptible to contamination.

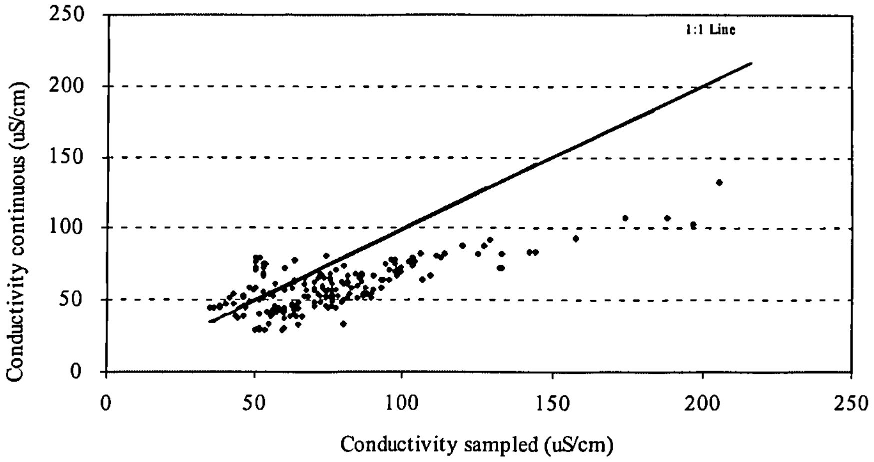
2. The automatic temperature correction on the Rosemount electrode has an operational window of 10^{oC} to 50^{oC} and at temperatures lower than 10^{oC} (frequent during winter) the temperature correction can be subject to error. All the test solution, buffers and the electrode were in thermal equilibrium before measurement or calibration were made.

3. Undissolved or biological materials deposits/films on the electrode present a barrier to measuring the true conductivity. This can be a major factor contributing to the uncertainty of the measurement, but can be controlled by regular maintenance.

4. Continuous conductivity field measurements are made under harsh conditions with low ionic strength stream water, temperature variations, algae, rapidly changing conductivity and a turbulent medium. Under such conditions, the electrode may be less sensitive, and errors can be introduced due to increased response time and noise. In contrast, laboratory measurements are made under ideal conditions and data are likely to be more accurate.

Comparing the continuous conductivity (C_c) against sampled conductivity (C_s), Figure 2.4, it was apparent there was a negative bias in the data (i.e. $C_c < C_s$). The bias appeared to increase at high conductivity generally associated with base-flow conditions. The bias exhibited by C_c ranged from 30 to 92.8 μScm^{-1} and was unexpected given the relative ease of conductivity measurements.

Figure 2.4 Sampled and continuous conductivity measurements



Conductivity measurement at Coalburn outfall was carried out at two distinct points. The continuous electrode and the auto-sampler measured conductivity in the weir pool, due to their infrastructure requirements. Routine samples were taken approximately 30m upstream at the gravel trap. The general differences in the sampling point characteristics and the location error evident in pH data was discussed in section 2.5.1.

On several occasions, the C_c electrode was used to measure the weir pool conductivity and a sample from the gravel trap upstream. As the same instrument was used for both measurements, the difference is likely to be attributable to the location error. This experiment demonstrated that under base-flow conditions the weir pool conductivity was less than in the natural channel for both the field and laboratory measurements (Table 2.7). The natural channel conductivity measured in the field and laboratory are similar which suggests there was no problem with the C_c electrode. In contrast, under high-flow/event conditions the conductivity measurements in the weir pool and natural channel are comparable (Table 2.7).

Table 2.7 Coalburn conductivity comparisons

Date	Continuous Electrode Conductivity in Weir Pool (μScm^{-1})	Continuous Electrode Conductivity of Upstream Sample (μScm^{-1})	Difference (μScm^{-1})	Conductivity Laboratory Sample (Gravel Trap) (μScm^{-1})	Flow (ls^{-1})
04 June 1997	86	137	-51	134	0.36
17 June 1997	39	49	-10	51	7.8
23 June 1997	38	47	-9	No data	13.5
01 July 1997	46	46	0	44	543
11 July 1997	56	74	-18	69	1.40
23 Sept 1997	37	53	-16	75	2.09

The location error in the C_c measurement could arise from: stagnation of water in the weir pool allowing suspended solids to fall out of suspension, the heterogeneity of sampling between the large weir pool and gravel trap, the lag time between the weir pool and gravel trap, the buffering capacity of the weir pool and other chemical changes due to retention time, temperature effects and interactions with the sediment/concrete.

Measurement of the conductivity at varying depths within the pool on 04 June 1997 revealed the weir pool could stratify during base-flow conditions with warm air temperatures. The surface conductivity was measured as $91\mu Scm^{-1}$, while at depth the conductivity was fifteen percent lower at 77 $\mu S/cm$, making the depth of measurement critical to the results representativity under these conditions. Therefore, measuring conductivity at one point maybe unrepresentative of the weir pool, and in turn that could be uncharacteristic of the catchment.

Similar to pH the C_c exhibits a diurnal variation during base-flow conditions when the temperatures are warm, the conductivity showing a strong positive relationship with temperature as the weir pool heated up.

The laboratory measured conductivity values are likely to reflect the true conductivity at Coalburn, while continuous field measurements involve a greater degree of uncertainty. Despite the negative bias in the C_c measurement the typical trace exhibits a smooth response (Chapter 4 and 5). This feature suggests the errors are highly auto-correlated and over the short to medium term the data may be systematically biased (Robson, 1993).

The C_c and C_s exhibits an approximately linear relationship (Figure 2.4); however, there is a large degree of scatter in the relationship, probably reflecting the effects of hysterisis and antecedent conditions (see Chapter 4). For example, during low flows conductivity values rise (as they can under high-flow conditions). Conductivity of the catchment water stores may change in time with catchment conditioning (Chapter 3, 4 and Robson, 1993). It is not surprising the same C_c value may be observed under contrasting flow/environmental conditions (that in turn effect the location error/bias).

A variety of corrections were derived to improve the validity of the C_c data, utilising temporal and flow splits etc. However, this analysis yielded poor results reflecting the wide spread in the data and contrasts in errors associated with event and base-flow conditions. To overcome this problem short-term event based corrections were derived for the conductivity to recognise the bias in the raw C_c data.

In summary, the sampled conductivity data are likely to be the most representative of Coalburn stream, despite sample decay, and should be treated as the **primary** source of numerical data. During base-flow conditions, the C_c in the weir pool exhibits a negative bias that increases as flow decrease arising from the location error. Current data suggests the location error diminishes under medium to high flows when there may be improved mixing and a reduced retention time in the weir pool.

Until further data are available, care should be taken when assuming the location error is minimal during medium to high flows and short-term event based corrections have been applied to the data where applicable.

The study proves that something as simple to measure as conductivity can be problematic when measured in the field and careful planning of the location of the electrode and auto-sampling equipment is essential.

2.6 Data analysis

2.6.1 Data quality assurance, storage and analysis

The raw data for the study are stored on the Environment Agency archives. The analysis of the data was carried out using Microsoft Excel and Minitab Version 12.21.

Before interpreting the rainfall, cloud mist and stream chemistry data in any depth, the data quality was checked. This was done using the charge balance techniques used by Stevens et al. (1997a). The charge balance alkalinity (CBALK) is calculated as:

$$\sum \text{Cations} = \sum \text{Anions}$$

$$\sum Ca + Mg + Na + K = \sum SO_4 + Cl + NO_3$$

Units in μEql^{-1}

For rainfall, cloudmist and river samples the CBALK was calculated where full/near full data sets were available and only missing values for potassium and nitrate were accepted as these contribute very little to the overall charge.

In summary, the analysis showed the data quality was satisfactory for the samples considered and where there was missing data it is likely these results will be satisfactory, as the same analysis procedures have been followed.

3 Coalburn: Hydrochemical patterns.

Overview

A substantial database of hydrochemical data has been gathered for the principal components of the Coalburn hydrological cycle. The focus of this chapter is to summarise this information and to identify the important chemical signatures, patterns and relationships the data illustrates for the Coalburn catchment. This analysis is based on the concentration data; chemical fluxes are examined, albeit in a relatively simplistic manner.

The aims and objectives of this research programme were outlined in Chapter 1. This chapter discusses the basic hydrochemical patterns in relation to these; examining the following topics:

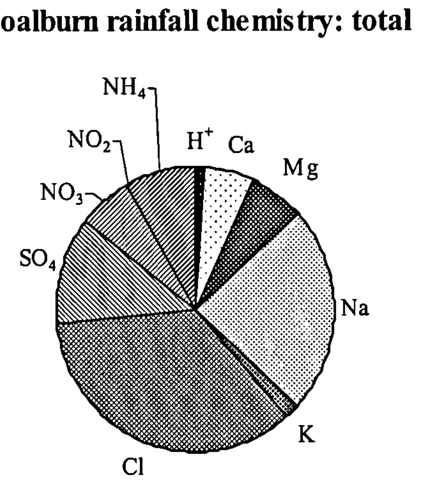
- *The results are comparable and elaborate on previous studies at Coalburn.*
- *The episodic acidification status of the Coalburn catchment can now be properly assessed.*
- *The data identify the important chemical signatures and hydrochemical variations (temporal and spatial) in the Coalburn rainfall, cloudmist and stream chemistries.*
- *A link can be established between stream chemistry and climate and chemical signatures.*
- *The hydrochemical variations can be can be explained by a combination of the catchment structure, biological factors, pollution climatology, flowpath and antecedent conditions.*

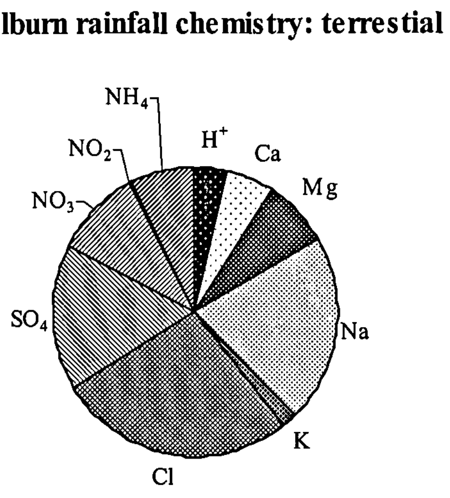
3.1 The nature and composition of rainfall

Rainfall at Coalburn is slightly acidic with a mean pH of 5.39 and its chemical composition similarly shows evidence of moderate pollution. The chemical composition is dominated by chloride and sodium ions, however, high concentrations of sulphate, nitrate and ammonium can occur (Figure 3.1, Tables 3.1 to 3.3). Generally, the southerly and westerly winds yield rainfall of low acidity and are associated with high concentration of marine ions (chloride, sodium, magnesium and sulphate) (Davies et al., 1992). In contrast, winds from the easterly sector yields rainfall with relatively low pH that is enriched with lithogenic and pollutant components (UKRGAR, 1990). The derivation of pollution climatology is discussed fully in section 3.4.

Chloride, sodium and magnesium in the rainfall are associated with marine sources and, while their concentrations show a wide range of variation, their ratios remain close to the seawater line (Figure 3.2). In contrast, sulphate, calcium and potassium are associated with both marine and terrestrial sources. These exhibit a composite pattern i.e. high concentrations of these ions can be associated with high chloride values due to the marine influence, or with low chloride values due to the input from terrestrial sources (Figure 3.2) (UKRGAR, 1990; Neal et al., 1992; Robson, 1993). Comparing the concentrations of non-marine sulphate, nitrate and ammonium observed with the reported UK ranges, it is evident that Coalburn receives moderate levels of acid deposition through the wet deposition pathway (Table 3.4). Furthermore, concentrations of these solutes plot above the seawater line, even those collected after spells of maritime influence. This suggests that deposition of pollutant ions must occur continually, although the amount varies according to weather conditions (Neal et al., 1992).

Figure 3.1 Coalburn rainfall: proportion of charge contributed by solutes





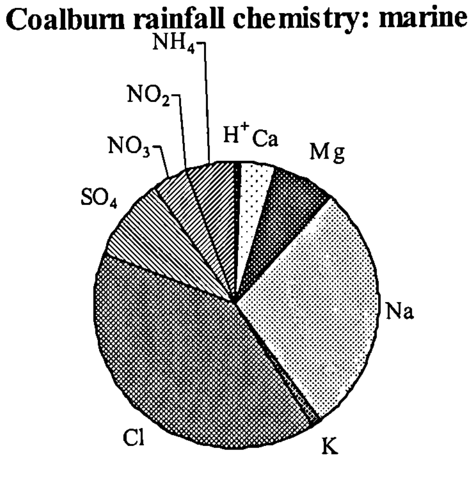
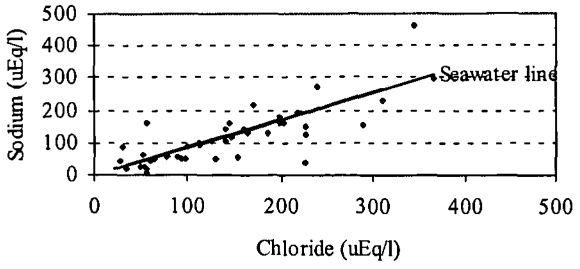
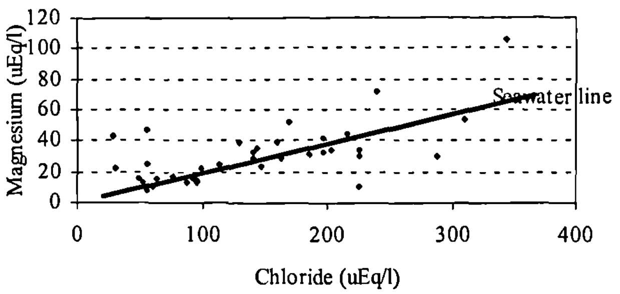
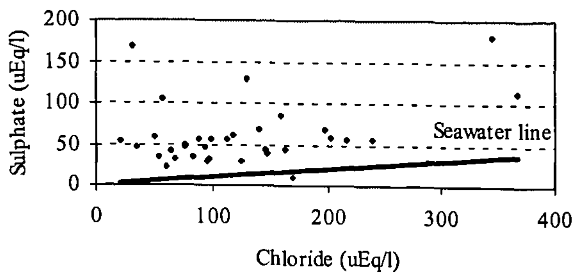
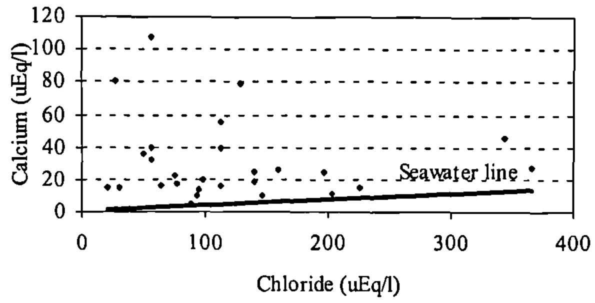


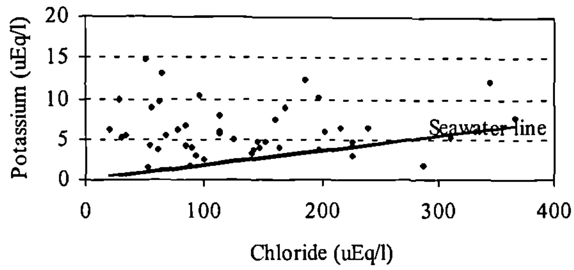
Figure 3.2 Ratio of solutes in rainfall compared with sea-water


Sodium


Magnesium


Sulphate


Calcium


Potassium

The rainfall concentration data were log transformed to normalise them and the variables cross-correlated to assess the relationships between the solutes (Table 3.5). Most correlation co-efficients are not significant reflecting the diverse sources of the ions in the rainfall chemistry. In addition, the two-week sampling period implies the bulk sample may be a product of several rainfall signatures.

The rainfall volume is inversely correlated with ammonium and nitrate. This could be attributed to a particle washout effect (Cresser and Edwards, 1987), however, it is more likely to be explained by high concentrations of these ions being associated with the easterly sectors that are in turn associated with low rainfall volumes.

The ion concentrations within the marine (Cl/Na/Mg) and terrestrial (SO_4/NH_4/NO_3) groupings tend to correlate strongly, as would be expected. Ammonium displays a negative relationship with chloride; however, the remainder of the marine and terrestrial ions do not exhibit an inverse relationship (i.e. the marine ions increase when terrestrial ions decrease and vice versa). Such direct relationships were perhaps not expected as the patterns are likely to be complicated by ions such as sulphate, calcium and potassium that can be derived from both sources.

The ratio of ammonium to non-marine sulphate ratio is 0.85, which is slightly higher than the UK mean of 0.6 (UKRGAR, 1990). This may reflect the proximity of Coalburn to Cumbria where livestock was identified as a major source of ammonium by the UKRGAR (1990). If the deposited ammonium is nitrified when it enters the catchment, this could be an important source of acidity (Van Breeman et al., 1982).

The concentrations and loads of sea salts ions exhibit some seasonality in their values with a peak in autumn/winter, coinciding with high rainfall volumes and progression of low pressure systems from the Atlantic; this is discussed later in Section 3.5.1.1.

Variability in rainfall chemistry implies that comparisons with other catchments produce results of little value, especially for marine ions that have a strong east to west gradient, reflecting proximity to the coast (UKRGAR, 1990). However, comparing the rainfall chemistry with the other Coalburn studies and the nearby Eskdalemuir meteorological site, it was noticeable the variability of ions observed in this study was not as great. For example, pH had a mean and range of 5.39 and 4.40 to 7.50 respectively, which can be compared to:

Eskdalemuir

1993	26 μEql^{-1} H^+	(Range: 0.3 to 199.5μeql^{-1} H^+)
	pH 4.6	(Range 3.70 to 6.52)

Other Coalburn Studies

Hind (1992)	62 μEql^{-1} H^+	(Range 0 to 154.9 μEql^{-1})
	pH 4.20	(Range 3.81 to 6.00)
Wake (1994)	18 μEql^{-1} H^+	(Range 1.99 to 100 μEql^{-1})
	pH 4.74	(Range 4.00 to 5.70)

There appears to be no significant relationship between calcium and pH (Table 3.5) suggesting that $CaCO_3$ interference could not account for the discrepancy. Furthermore, the laboratories are NAMAS accredited and have quality control systems; indeed an independent audit validated the analytical techniques. The main difference between this and previous surveys was the sampling frequency. Coalburn was sampled monthly up to February 1994 and thereafter twice monthly. The other studies involved weekly sampling. The effect of this is demonstrated in the 1993 data, which is less acidic and has less variation when compared to the other years (Table 3.6). The apparently smoothed input signature probably reflects the composite nature of the sample.

Consequently, the results presented in Tables 3.1 to 3.3 may not include 'extreme' events in rainfall chemistry at Coalburn and more intense data collection would be required to fully validate the extreme rainfall chemistry. Nevertheless, the data are sufficient to identify the significant inputs and patterns.

Table 3.1 Summary of Coalburn rainfall chemistry

	Mean VW	Maximum	Minimum	Number
pH	5.39	7.50	4.40	94
Hydrogen	4.08	39.81	0.03	94
Al	0.85	1.68	0.42	12
Ca	25.4	107.8	3.5	36
Mg	26.8	105.3	5.8	61
Na	97.9	465.5	6.1	70
K	7.8	97.2	0.5	83
Cl	144.5	366.7	20.9	58
SO_4	51.5	181.6	10.4	58
$nmSO_4$	46.7	165.4	1.6	57
NO_3	26.4	125.5	2.7	64
NO_2	0.50	1.93	0.01	45
NH_4	33.4	105.7	5.6	97
DOC	2.1	8.6	0.3	70
TOC	1.5	8.7	0.3	43
Colour	5.5	29.0	0.5	66
Mn	0.57	1.74	0.49	8
Fe	0.49	1.20	0.29	11
Conductivity	29.6	78	12	64
Volume	64	361.9	1.9	105

Table 3.2 Summary of Coalburn rainfall chemistry: marine signature

	Mean VW	Maximum	Minimum	Number
pH	5.71	7.30	5.19	31
Hydrogen	1.94	6.31	0.05	31
Al	0.77	no data	no data	1
Ca	17.1	35.9	5.5	6
Mg	27.7	54.2	9.7	21
Na	113.6	231.4	22.6	24
K	4.9	70.1	1.5	28
Cl	159.9	310.3	49.9	24
SO_4	38	68.9	10.4	20
$nmSO_4$	34.7	67.5	1.6	19
NO_3	16.3	42.9	2.7	20
NO_2	0.22	1.14	0.06	20
NH_4	22.6	99.0	5.6	35
DOC	2.3	7.5	0.3	28
TOC	1.3	3.0	0.4	13
Colour	4.2	13.7	1.0	23
Mn	0.37	no data	no data	1
Fe	no data	no data	no data	no data
Conductivity	23.0	42.0	12.0	18
Volume	69.9	173.6	10.4	36

Key to above tables

VW = Volume weighted.

Units: all units are in μEql^{-1} except: Al and Fe are in $\mu Moll^{-1}$; DOC, TOC and Colour in mgl^{-1}, Conductivity in μScm^{-1}. Volume = rainfall areal average in mm. $nmSO_4$ – the total sulphate value corrected using the sea water chloride to sulphate ratio, and this represents non-marine sulphate attributable to anthropogenic and natural processes excluding sea spray.

Table 3.3 Summary of Coalburn rainfall chemistry: terrestrial signature

	Mean VW	Maximum	Minimum	Number
pH	4.81	5.69	4.50	17
Hydrogen	15.53	31.62	2.00	17
Al	0.71	0.89	0.46	5
Ca	22.6	107.8	10.5	8
Mg	30.9	69.1	10.9	8
Na	88.0	293.6	6.1	10
K	6.4	46.0	3.1	12
Cl	112.1	366.7	20.9	13
SO_4	66.9	168.6	21.9	11
nmSO_4	57.6	165.5	158.8	11
NO_3	42.3	125.5	156.6	11
NO_2	0.14	0.71	0.01	5
NH_4	30.5	105.7	7.7	15
DOC	2.7	8.6	0.5	12
TOC	1.4	3.7	0.3	11
Colour	4.7	29.0	1.5	11
Mn	0.42	no data	no data	1
Fe	0.36	0.46	0.18	2
Conductivity	23.9	59.0	13.0	12
Volume	26.0	94.0	1.9	19

Key to above table

VW = Volume weighted.

Units: all units are in μEql^{-1} except: Al and Fe are in μMoll^{-1}; DOC, TOC and Colour in mgl^{-1}, Conductivity in μScm^{-1}. Volume = rainfall areal average in mm. nmSO_4 – the total sulphate value corrected using the sea water chloride to sulphate ratio, and this represents non-marine sulphate attributable to anthropogenic and natural processes excluding sea spray.

Table 3.4 Comparison of Coalburn rainfall chemistry with UK ranges

Solute	Coalburn Mean	UK Range
Non-marine sulphate	46.7	<20 to >100
Nitrate	26.4	<20 to >40
Ammonium	33.4	<10 to >50

Concentrations μEql^{-1}

Data from Neal et al. (1996)

Table 3.5 Rainfall solutes concentration correlations

	Vol	pH	H^+	Colour	Cond	NH_4	NO_3	NO_2	Cl	SO_4	Na	K	Mg	Ca	DOC	TOC	Al	Mn	Fe
Volume																			
pH	ns																		
H^+	ns	-***																	
Colour	-**	ns	ns																
Cond	ns	ns	ns	**															
NH_4	-**	ns	ns	**	***														
NO_3	-**	ns	ns	*	***	***													
NO_2	ns	***	***	ns	**	***	**												
Cl	ns	ns	ns	-*	**	ns	ns	ns											
SO_4	ns	ns	ns	ns	***	***	***	ns	ns										
Na	ns	ns	ns	ns	**	ns	ns	ns	***	ns									
K	-***	ns	ns	**	ns	**	**	ns	ns	**	ns								
Mg	ns	ns	ns	ns	***	ns	ns	ns	***	***	***	**							
Ca	ns	ns	ns	ns	ns	*	**	ns	ns	***	ns	***	**						
DOC	ns	ns	ns	ns	ns	***	***	ns	ns	***	ns	ns	ns	***					
TOC	-**	ns	ns	***	ns	*	ns	ns	ns	*	ns	**	ns	**	***				
Al	ns	ns	ns	ns	ns	ns	ns	ns	ns	ns	ns	ns	*	ns	ns	ns			
Mn	ns	ns	ns	ns	ns	ns	ns	ns	ns	ns	ns	ns	ns	ns	ns	ns	ns		
Fe	ns	ns	ns	ns	ns	ns	ns	ns	ns	ns	ns	ns	**	ns	ns	ns	ns	ns	

Key

$p > 0.05$	ns	- Negative correlation
$p < 0.05$	*	
$p < 0.01$	**	
$p < 0.001$	***	

Table 3.6 Comparison of pH means and sampling frequency for rainfall

Year	H^+ Mean	pH Mean	Max pH	Min pH	Number
93	0.56	6.25	7.50	6.00	12
94	3.98	5.40	7.30	4.50	20
95	2.81	5.55	6.50	5.10	20
96	8.20	5.09	6.30	4.40	18
97	5.50	5.26	6.70	4.50	24
93-97	4.98	5.30	7.30	4.40	82
94-97	4.08	5.39	4.40	7.50	94

Units H^+ μEql^{-1}, pH unitless

3.2 The nature and composition of cloud mist

Preliminary results indicate that cloud deposition at Coalburn occurs for approximately 500 hours per annum, which equates to an annual input of 50-90mm to the water balance (Robinson et al, 1998). However, while the volumetric contribution of cloud mist to the water balance is relatively small; the high concentrations of solutes observed in this pathway make it a potentially important flux to the ecosystem.

The solute concentrations are summarised in Tables 3.7 to 3.9 and Figure 3.3; volume weighting was not possible and the arithmetic, median and geometric means are presented. The geometric mean and median are given as an indication of a central value because many of the solute distributions are log normal and/or skewed by infrequent large values.

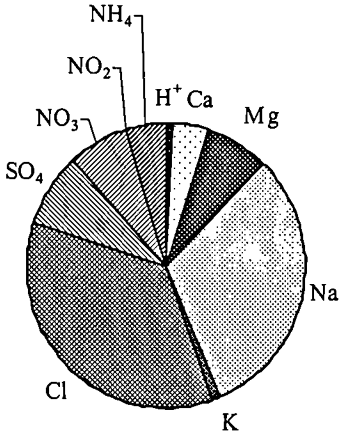
The cloud mist at Coalburn was more acidic than rainfall (with a mean pH of 4.26) and its chemical composition showed considerable variability reflecting the different sources from which it is derived (Tables 3.7 to 3.9). The average composition of cloud mist was dominated by marine ions (Cl: 0.50g/l; Na: 0.47g/l), however, high concentrations of acidic ions can occur (SO_4: 0.15g/l; NO_3: 0.42 g/l; NH_4: 0.03 g/l).

Chloride, sodium and magnesium ratios in the cloud mist were close to the seawater line, reflecting the marine influence at Coalburn (Figure 3.4). Similar to the rainfall chemistry sulphate and calcium demonstrate a composite pattern, as they were associated with both marine inputs and terrestrial inputs. Sulphate concentrations had a positive bias indicating that cloud mist is a potential pathway for acid deposition even during periods when marine influences were dominating (Figure 3.4).

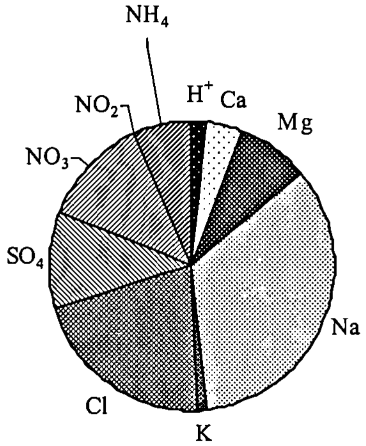
The data were log transformed to normalise them and the ions correlated to assess the relationships between the data (Table 3.10).

Figure 3.3 Coalburn cloud mist: proportion of charge contributed by solutes

Coalburn cloud mist chemistry



Coalburn cloud mist chemistry: terrestial



Coalburn cloud mist chemistry: marine

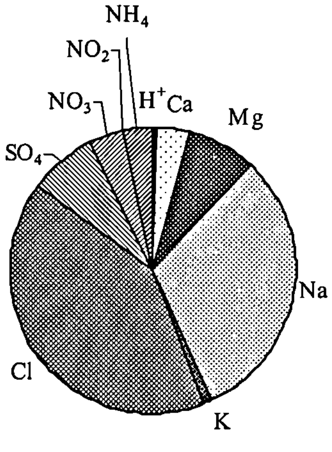
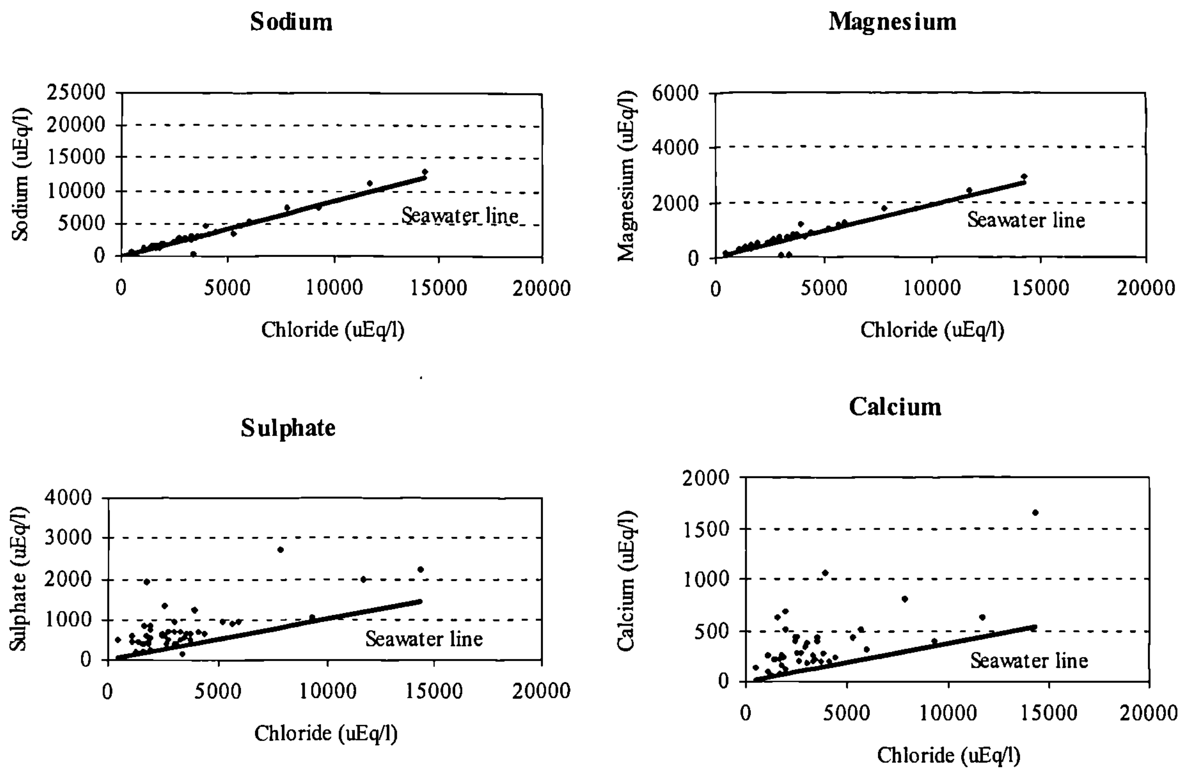


Figure 3.4 Ratio of solutes in cloud mist compared with sea-water



The cloud mist data exhibits similar patterns to the rainfall, with the marine and terrestrial ions being significantly correlated. The total and dissolved organic carbon exhibit significant correlation with ammonium, nitrate and the metals. The most likely source of total/dissolved organic carbon in the atmosphere are terrestrial sources such as un-combusted and combusted fuels and they will be associated within other pollutant ions (UKRGAR, 1990). There was no evidence of an inverse relationship between the marine and terrestrial ions but such patterns are complicated by ions such as sulphate, calcium and potassium that can be derived from both sources.

Cloud mist concentrations were enriched compared to those of rainfall. The average enrichment factor was eleven times and ranges from 2 (NO_2) to 24 (Na) (Table 3.15). These values are similar to those observed by Wilkinson et al. (1997). Comparing the means and range of values for the rainfall and cloud mist (Table 3.1 and 3.7) it is apparent that the cloud mist exhibits more variability than the rainfall.

The enrichment of cloud mist occurs partly because it is derived from the bottom layer of cloud. The base layer of a cloud has higher concentrations of solutes which rapidly decrease with height reflecting the adiabatic increase in liquid content of the cloud with altitude (Fowler, 1989; UKRGAR, 1990; Wilkinson et al., 1997). However, some of the enrichment may be an artefact of the sampling equipment:

- High wind-speed aerodynamically sorts raindrop size, with the smaller drops preferentially carried to the collector. Smaller drops are associated with higher concentrations and this may enhance the cloud mist concentrations, as the rainfall collector will not collect these drops as efficiently (Wilkinson et al., 1997).

- Cloud mist collectors are subject to dry/particulate deposition between and during cloud and rain events. Dry and particulate deposition also affect the rainfall collectors but the physical structure of the cloud collector makes it more effective at scavenging than the rainfall collector.

- Evaporation of cloud drops from the collector strings may also occur leading to enhanced solute concentrations, although Milne (1988) indicated this is likely to be relatively small.

- There will be some degree of rainwater contamination during periods when the wind speed was greater than 5 ms^{-1}.

Table 3.7 Summary of Coalburn cloud mist chemistry

	Mean	Median	Geomean	Maximum	Minimum	Number
pH	4.26	5.20	5.21	7.20	3.00	53
Hydrogen	54.5	6.3	6.1	1000	0.1	53
Al	13.5	14.2	8.7	28.1	1.1	10
Ca	393	280	308	1657	63	48
Mg	788	551	569	4791	58	48
Na	3296	2392	2389	20445	182	49
K	91	71	70	484	3	49
Cl	3381	2624	2687	14330	466	57
SO_4	796	625	641	3061	125	51
nmSO_4	410	315	291	1925	35	46
NO_3	871	548	521	6764	40	54
NO_2	2.9	1.0	1.0	51.6	0.1	48
NH_4	497	367	363	1622	40	55
DOC	6.8	4.7	4.9	30.6	1.1	35
TOC	6.3	5.4	5.0	23.7	0.9	31
Colour	15.4	9	10.1	98.9	1.5	42
Mn	1.7	1.4	1.5	4.1	0.8	10
Fe	10.9	13.3	7.7	19.0	1.6	7
Conductivity	586	475	486	2396	77	41

Table 3.8 Summary of Coalburn cloud mist chemistry: marine signature

	Mean	Median	Geomean	Maximum	Minimum	Number
pH	4.76	5.44	5.54	6.90	3.70	20
Hydrogen	17.3	3.6	2.9	199.5	0.1	20
Al	3.9	3.2	2.9	7.3	1.1	3
Ca	304	261	260	683	80	20
Mg	652	603	539	1749	58	20
Na	2624	2570	2133	7525	182	21
K	68	64	55	173	2.6	21
Cl	3164	1777	2787	9281	1100	25
SO_4	567	591	504	1024	125	23
nmSO_4	264	241	202	703	35	22
NO_3	379	317	262	1623	40	25
NO_2	1.7	0.8	0.9	11.6	0.2	22
NH_4	310	257	230	1054	40	24
DOC	3.7	3.5	3.3	7.0	1.1	18
TOC	4.7	4.4	4.1	10.1	1.2	14
Colour	8.8	6.5	7.0	24.0	1.5	16
Mn	1.1	1	1.1	1.4	0.9	3
Fe	15.6	15.6	15.6	no data	no data	1
Conductivity	521	499	479	1100	233	14

Key to above tables

VW = Volume weighted.

Units: all units are in μEql^{-1} except: Al and Fe are in $\mu Moll^{-1}$; DOC, TOC and Colour in mgl^{-1}, Conductivity in μScm^{-1}. nmSO_4 – the total sulphate value corrected using the sea water chloride to sulphate ratio, and this represents non-marine sulphate attributable to anthropogenic and natural processes excluding sea spray.

Table 3.9 Summary of Coalburn cloud mist chemistry: terrestrial signature

	Mean	Median	Geomean	Maximum	Minimum	Number
pH	3.77	4.86	4.56	5.80	3.00	10
Hydrogen	166.8	13.7	27.5	1000	1.6	10
Al	23.6	21.6	23.4	28.1	23.6	3
Ca	540	429	439	1367	190	9
Mg	1196	622	805	4791	349	9
Na	4994	2488	3253	20445	1466	9
K	135	83	102	484	52	9
Cl	2826	2595	2131	7814	682	9
SO_4	1392	1151	1094	3061	387	9
$nmSO_4$	928	742	609	1925	146	6
NO_3	1417	1339	1248	2336	475	8
NO_2	4.4	1.1	1.1	24.3	0.1	7
NH_4	576	1103	676	1622	187	9
DOC	15.1	15.1	14.8	18.3	11.9	2
TOC	13.4	13.9	9.5	23.7	2.6	3
Colour	18.1	9.4	12.1	79.0	7	8
Mn	2.9	2.6	2.8	4.1	2.9	2
Fe	14.4	17.9	12.9	18.9	6.3	3
Conductivity	720	466	578	2396	266	10

Key to above table

VW = Volume weighted.

Units: all units are in μEql^{-1} except: Al and Fe are in $\mu Moll^{-1}$; DOC, TOC and Colour in mgl^{-1}, Conductivity in μScm^{-1}. $nmSO_4$ – the total sulphate value corrected using the sea water chloride to sulphate ratio, and this represents non-marine sulphate attributable to anthropogenic and natural processes excluding sea spray.

Table 3.10 Cloud mist solutes concentrations correlation

	pH	H	Colour	Cond	NH_4	NO_3	NO_2	Cl	SO_4	Na	K	Mg	Ca	DOC	TOC	Al	Mn	Fe
pH																		
H	-***																	
Colour	ns	ns																
Cond	ns	ns	ns															
NH_4	-**	+**	+**	ns														
NO_3	-*	+*	+**	ns	+***													
NO_2	ns	ns	ns	ns	ns	ns												
Cl	ns	ns	ns	+*	ns	ns	ns											
SO_4	ns	ns	ns	+**	+***	+***	ns	+***										
Na	ns	ns	ns	+**	ns	+*	ns	+***	+***									
K	ns	ns	ns	+**	+*	+***	ns	+***	+***	+***								
Mg	ns	ns	ns	+*	ns	+*	ns	+***	+***	+***	+***							
Ca	ns	ns	ns	+**	+***	+***	ns	+***	+***	+***	+***	+***						
DOC	ns	ns	+***	ns	+***	+***	ns	ns	+***	+**	+**	+*	+***					
TOC	ns	ns	+**	ns	+***	+***	ns	ns	+***	ns	+**	ns	+***	+***				
Al	-*	+*	ns	ns	ns	ns	ns	ns	ns	ns	ns	ns	*ns*	*ns*	*ns*			
Mn	ns	ns	ns	ns	+***	+***	ns	ns	+**	ns	ns	+*	+**	+*	+*	+*		
Fe	ns	ns	ns	ns	ns	ns	ns	ns	ns	ns	ns	ns	ns	ns	ns	ns	ns	

Key			
	$p > 0.05$	ns	- Negative correlation
	$p < 0.05$	*	
	$p < 0.01$	**	
	$p < 0.001$	***	

3.3 The nature and composition of dry deposition

During dry periods the principal pathway of atmospheric ions to the catchment will be through dry and gaseous deposition, this will be further enhanced at Coalburn by the 'scavenging' efficiency of conifers (Department of Environment and Forestry Commission, 1990; Reynolds et al., 1989). Consequently, any interpretation of the catchment response must take into account the 'conditioning' effect of dry deposition.

Dry deposition was not measured at Coalburn and remains unknown in this study. However, it is likely to be most important when high pressure prevails, with little vertical mixing and light winds from the easterly sectors. These winds will be enriched with terrestrial/acidic ions and through dry deposition some will enter the Coalburn catchment and may effect the subsequent catchment response/processes (Fowler et al., 1989).

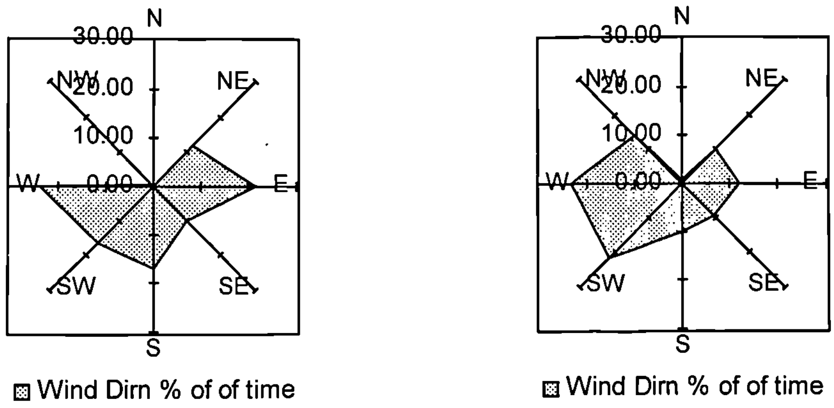
In this study, it is inferred that when wet and cloud deposition ceases a dry deposition component will begin of a similar chemical signature. Observations by Wake (1994) suggested this is a valid assumption at Coalburn and allowed her to identify the importance of dry intervals in conditioning the stemflow and interception chemistries.

3.4 Pollution climatology

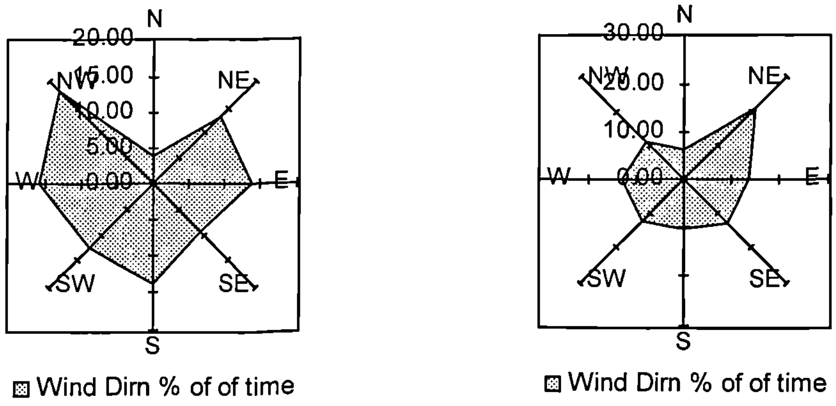
Wind direction and the duration of air flow from that direction have a significant bearing upon the input of ions from the atmosphere by wet, dry and occult deposition (Davies et al., 1992). This section examines the 'pollution climatology' for Coalburn by back tracking through the dominant antecedent wind direction and attributing the chemistry observed in the rainfall and cloud mist to a likely source area. The study can only consider rainfall and cloud mist; however, it can be inferred that when the wet deposition ceases, dry deposition of a similar chemical signature is likely to begin.

Sector plots (Figure 3.5) derived from Coalburn AWS data demonstrate the wind direction is predominantly from marine sources (i.e. the west and south west), reflecting the importance of frontal weather systems in the UK. However, the diagrams also indicate there are periods when wind from the easterly sectors can dominate. The study period includes the 1995/1996 drought and winter snowfall during which extended periods of weather were dominated by the easterly sectors (Figure 3.5).

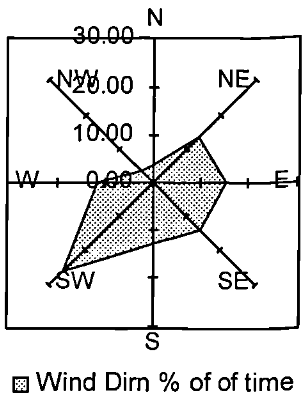
Figure 3.5 Wind direction sector plots


93 Wind Direction Summary

94 Wind Direction Summary


95 Wind Direction Summary

96 Wind Direction Summary


97 Wind Direction Summary

The back tracking of trajectories carries with it several intrinsic uncertainties, firstly the surface wind direction can be different depending upon the scale of observation and the altitude considered (Newson, 1986; UKRGAR, 1990). Therefore, while the Coalburn AWS data reflects the micro-climate of the Coalburn catchment, the meso-scale wind patterns may be the dominant control over the pollution climatology. In the presence of a frontal system, the situation becomes more complex, and the solute flux will change not only with wind direction but also according to the air-mass type as the front passes.

For each sampling period, the dominant wind direction(s) was assessed using the AWS data and the meso-scale weather patterns determined from the Met. Office daily weather charts. The periods were then classified into two generic groups according to origin; 'marine' and 'terrestrial'. 'Marine' winds occur from the south west, west and north west whilst 'terrestrial' winds occur from the east, south east and north east sectors. Winds from the north and south were excluded as they could have originated from either source. Deposition periods were classified only if the period was dominated by winds from those sectors; thus, a period where the pollution climatology was composite in nature (e.g. frontal systems) was not classified.

For both rainfall and cloud mist a marine and terrestrial chemical signature was determined (Tables 3.1 to 3.3 and 3.7 to 3.9). The marine signature typically has a high pH and elevated concentration of marine ions (chloride, sodium, magnesium and potassium). In contrast, the terrestrial signature reflects its path over agricultural land and industrial areas in Britain and/or further east in Europe. Consequently, the easterly direction yields wet deposition with low pH and enriched lithogenic and pollutant components (Davies et al., 1990; Reynolds et al., 1989).

The difference between the 'marine' and 'terrestrial signatures can be seen in Figures 3.1 and 3.3, and the comparisons of the solute concentration of each signature were compared statistically using a t-test. For the rainfall chemistry, the analysis revealed the volume, pH and nitrate concentrations were significantly different between the two signatures ($p < 0.005$). The sulphate concentrations were different but at a significance level of $p = 0.077$. The other solutes were not significantly different, and this may be accounted for by the fact that many solutes can be derived from both sources.

The cloud mist t-tests revealed the pH, ammonia, nitrate and sulphate concentrations were significantly different ($p < 0.05$), with the other solutes showing no significant difference. It was noticeable that the solutes that exhibit a difference are associated with the anthropogenic component of the terrestrial signature. In contrast, there is no difference with the sea-salts suggesting that even when the winds are from the easterly sectors a component of the marine signature is still evident in the chemistry.

Thus, the antecedent pollution climatology is likely to influence the input signal to the catchment and be an important factor when considering the processes that underlie the hydrochemical response in the stream. Furthermore, it demonstrates that periods of acid and marine deposition can 'impact' on the catchment, implying both anthropogenic pollutants and sea-salt events could be important processes behind acid events at Coalburn.

3.5 The nature and composition of streamwater chemistry

3.5.1 Coalburn streamwater quality

Coalburn streamwater chemistry generally shows higher concentrations of solutes than the rainfall, reflecting the chemical and biological reactions occurring in the catchment as well as the cloud water and dry deposition inputs. Streamwater chemistry has relatively low ionic strength and varies from being well buffered to acidic (Table 3.11, Figure 3.6). In terms of acidification, Coalburn can be defined as a transitional site (Ferrier and Harriman, 1990), i.e. it has positive Acid Neutralising Capacity (ANC) at low flow and a negative ANC at high-flow but retains a fish/invertebrate population (Prigg, 1994 & 1999: Appendix J). The flow weighted mean pH of 4.47 is acidic but this figure would appear to be skewed by the over representation of event samples and this should be borne in mind when assessing this and the other chemical solutes. The main ions contributing to the Coalburn streamwater chemistry are chloride and sodium, derived from marine origins (Figure 3.6), with their ratio's remaining approximate to those in seawater. Sulphate and calcium make up a significant proportion of the streamwater ionic charge (Figure 3.6), more so than in the rainfall, suggesting catchment processes (e.g. scavenging, retention, weathering etc.) have an important influence on these components. The remaining ions make only a relatively minor contribution to the overall charge.

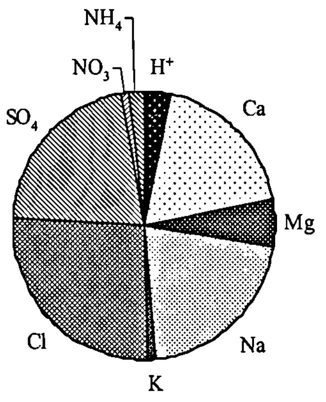
Most solute concentrations do not vary strongly with flow, typically varying by only one order of magnitude, whilst flow may vary by four orders of magnitude. However, some chemical solutes exhibit a marked dependency on streamflow: conductivity, pH, colour, iron, calcium and magnesium demonstrate an inverse relationship with flow. Nitrate, ammonia, chloride, sulphate, manganese and aluminium show a positive relationship (Table 3.12 and Figure 3.7). Typically the major concentration changes occur at low flows (0 to 20 ls^{-1}); at intermediate and high flows concentrations remain constant or decline as flow increases (Figure 3.7). While these patterns are related to changing flow, it is the catchment's physical structure, hydrological pathways, antecedent and event conditions that really lies behind such patterns.

The data were log transformed to normalise them and the variables cross-correlated to assess the relationships between the solutes (Table 3.12). It is apparent that, while the streamwater chemistry is variable, there are strong inter-relationships between some solutes. The relative contributions and relationships between solutes vary according to the physical structure of the catchment, the source of solutes, chemical and biological processes, flow, season and climate. The following sections discuss the patterns observed at Coalburn, broadly classifying them according to:

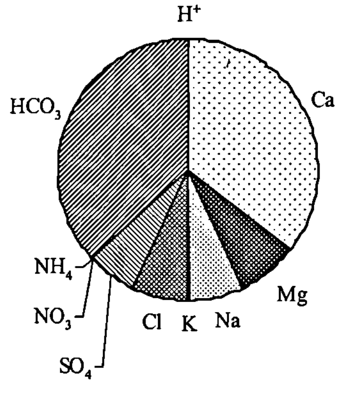
- The atmospheric component.
- Weathering and inorganic component.
- Nutrient and biologically mediated component.

Figure 3.6 Coalburn stream: proportion of charge contributed by solutes

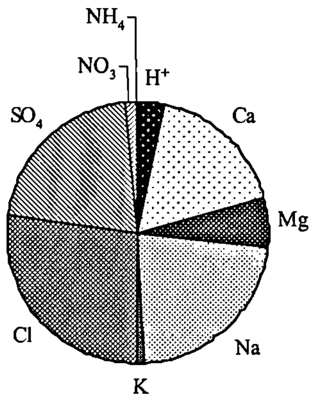
Coalburn stream chemistry



Coalburn stream chemistry: base flow



Coalburn stream chemistry: high flow



Note: HCO_3 is not included in the total and high flow pie as it is only a minor component (<0.1%).

Figure 3.7 Relationship between some solutes and streamflow

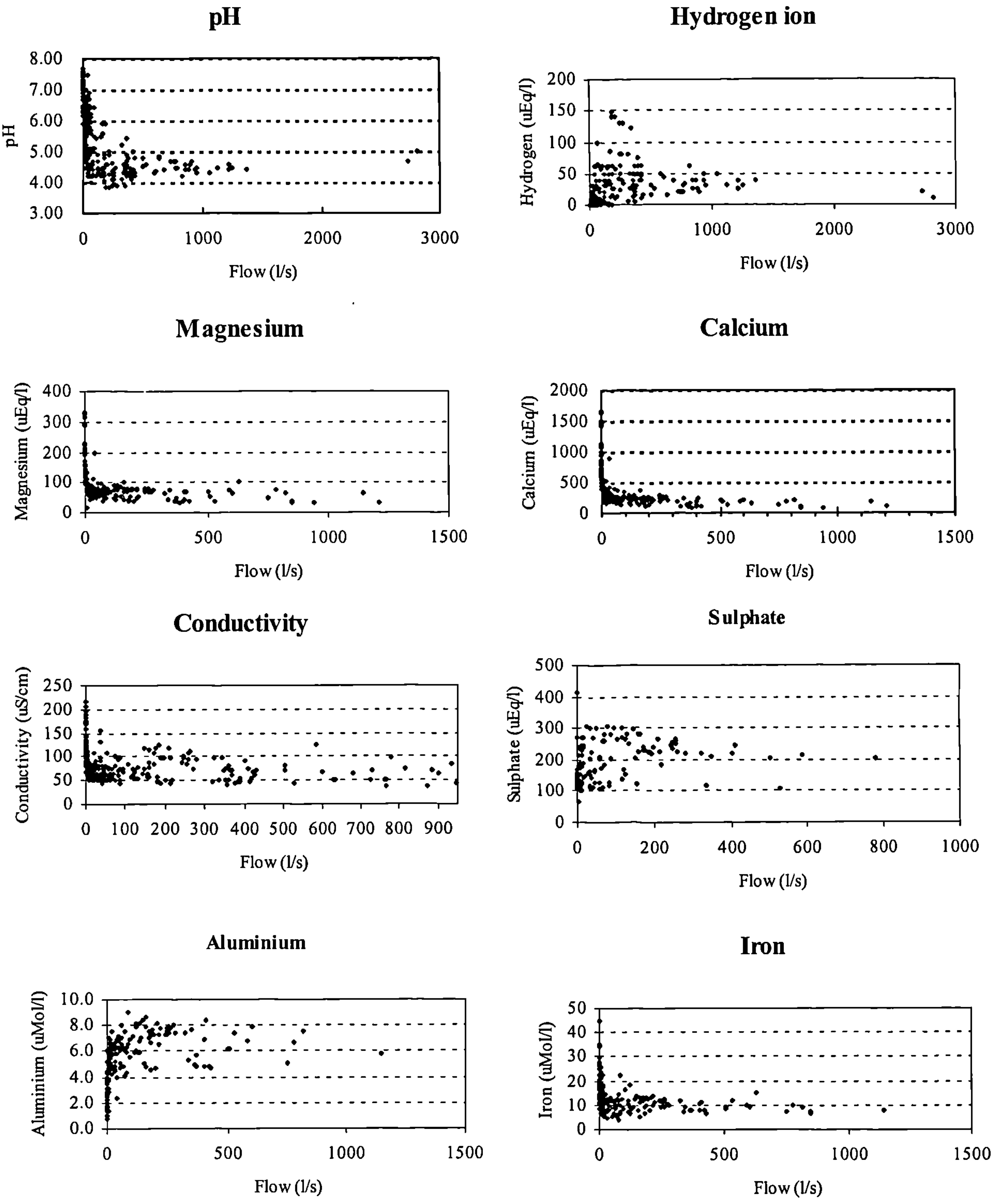


Table 3.11 Summary of Coalburn stream, baseflow and storm flow chemistry

	Coalburn	Baseflow	Storm flow
pH	4.47	7.22	4.53
	(7.49-3.30)	(7.06-8.82)	(5.00-4.21)
Hydrogen	34.02	0.06	29.83
	(147.91-0.02)	(0.087-0.001)	(61.66-10.)
Al	6.5	2.1	6.5
	(9.0-0.3)	(2.7-0.8)	(7.9-5.0)
Ca	186	1044	149
	(1652-88)	1652-739)	(215-88)
Mg	60	219	54
	(328-17)	(328-160)	(99-31)
Na	208	198	193
	(331-70)	(224-172)	(251-145)
K	7.6	6.8	9.9
	(36.1-1.0)	(18.7-2.6)	(25.1-3.3)
Cl	266	207	237
	(437-113)	(238-141)	(309-113)
SO_4	215	177	184
	(412-68)	(412-214)	(212-107)
NO_3	7.4	0.71	11.6
	(25.2-0.02)	(1.4-0.06)	(25.2-1.0)
NH_4	2.6	1.5	3.1
	(5.3-0.3)	(2.7-0.7)	(5.3-1.4)
DOC	18.5	19.3	15.9
	(33.9-7.4)	(27.9-11.9)	(23.8-10.6)
TOC	21.7	19.7	21.0
	(33.9-9.7)	(27.5-15.1)	(24.2-19.1)
Colour	112	149	103
	(327-38)	(245-38)	(178-63)
Mn	1.0	1.0	1.2
	(2.4-0.4)	(2.1-0.5)	(1.6-0.6)
Fe	9.8	20.7	9.1
	(44.8-1.2)	(44.8-10.4)	(15.2-6.7)
Conductivity	61.9	138.4	53.8
	(205.7-34.5)	(216-106)	(125-34.5)
SiO_2	1.9	2.3	1.7
	(3.9-1.0)	(3.2-1.4)	(2.1-1.1)
Flow	177.5	0.39	940
	(2814-0.08)	(0.68-0.08)	(2814-502)

All means are flow weighted.

Units All units are in μEql^{-1} except:
Al and Fe are in μMoll^{-1}; DOC, TOC, SiO_2 and Colour in mgl^{-1}
Conductivity in μScm^{-1}
Flow in ls^{-1}

Table 3.12 Coalburn stream solute concentration correlation

	Flow	pH	Colour	Cond	NH_4	NO_3	NO_2	Cl	SO_4	Na	K	Mg	Ca	DOC	TOC	Al	Mn	Fe
Flow																		
pH	-***																	
Colour	-***	***																
Cond'y	-***	***	ns															
NH_4	***	-***	ns	ns														
NO_3	***	-**	ns	ns	ns													
NO_2	ns	ns	ns	ns	ns	**												
Cl	***	-***	-***	**	ns	*	-***											
SO_4	***	-***	-***	***	ns	**	-*	***										
Na	ns	-***	-**	***	ns	ns	-***	***	***									
K	ns	ns	ns	***	*	**	ns	ns	ns	ns								
Mg	-***	***	ns	***	-***	ns	-**	ns	ns	***	*							
Ca	-***	***	**	***	-***	-*	-*	-**	-*	ns	ns	***						
DOC	ns	ns	***	ns	ns	ns	***	-**	-***	-***	ns	ns	ns					
TOC	ns	ns	***	-*	ns	ns	ns	-***	ns	ns	ns	ns	ns	***				
Al	***	-***	ns	-***	***	**	ns	***	**	*	ns	-***	-***	***	*			
Mn	ns	ns	ns	***	ns	**	ns	ns	**	**	**	***	***	***	*	ns		
Fe	-***	***	***	ns	ns	-*	ns	-***	-***	-**	ns	***	***	***	***	-***	***	

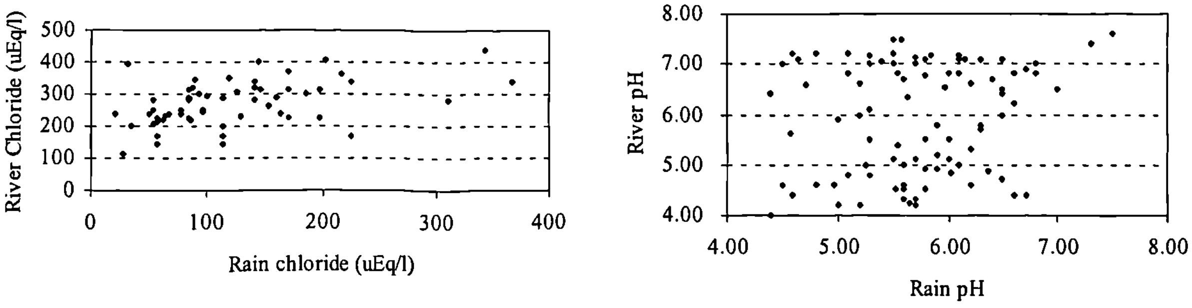
Key
$p > 0.05$ ns
$p < 0.05$ *
$p < 0.01$ **
$p < 0.001$ ***
- Negative correlation

3.5.1.1 Atmospheric Component

Coalburn stream flow reacts rapidly to rainfall; given this characteristic it might have been anticipated that the stream chemistry would respond in a similar manner. However, there was generally no short-term direct link between rainfall and stream chemistry even for unreactive components such as chloride (Figure 3.8) (Reynolds et al., 1997; Robinson et al., 1994; Neal et al., 1992). This implies the catchment has the ability to smooth/damp the rainfall signal and terrestrial processes modifying the rainfall signal to produce the observed stream chemistry. Similarly for the reactive solutes, there were no short-term links between the rainfall and stream chemistry. For example, the pH response is dominantly controlled by flow and reflects the within catchment gradients. Even during hydrological events on a saturated catchment these gradients dominate, suggesting that pH is rapidly modified by terrestrial process to produce the catchment response.

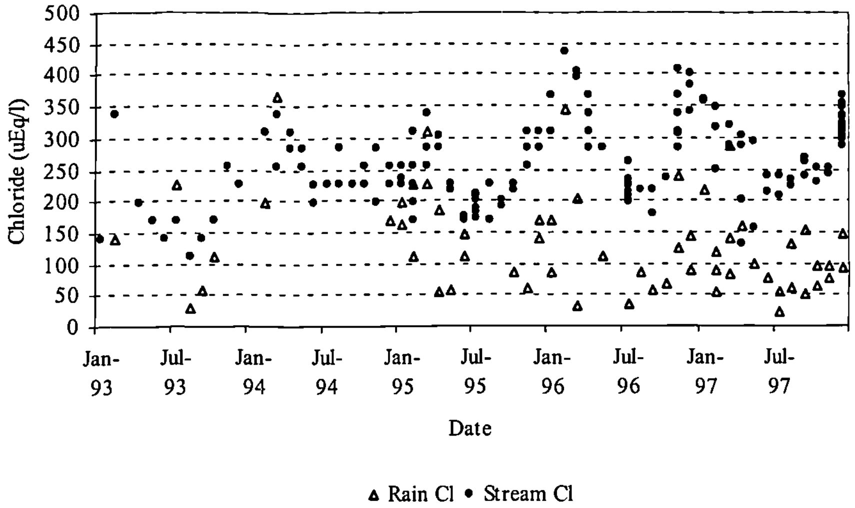
While the Coalburn stream and rainfall chemistries are not apparently directly linked on a short-term timescale the true situation is more complex. Chloride in Coalburn streamwater is primarily from marine origins, through the wet and dry deposition pathway that exhibits a seasonal pattern. This pattern is mirrored in the streamwater chemistry, although the response is damped (Figure 3.8).

Figure 3.8 Comparison of rainfall and stream chemistry

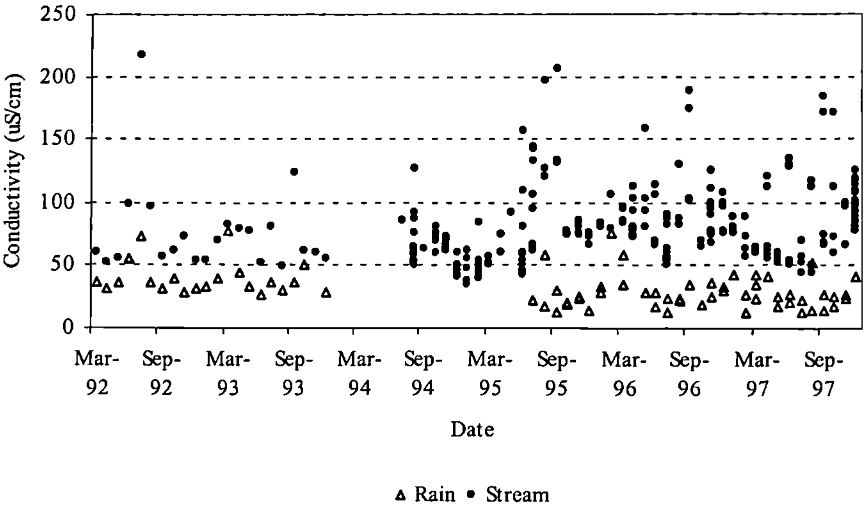

Chloride

pH

Chloride rainfall and stream concentration time series



Conductivity rainfall and stream time series



The lag between the peak rainfall and streamwater concentration/load appears to be dependent upon the magnitude of the hydrological and chemical signature. For example, rainfall samples on 14 February 1996 and 01 March 1995 had the highest chloride concentrations observed in the study and the stream concentrations indicate an almost instantaneous response followed by a gradual decline (Figure 3.8). During large hydrological events, with wet antecedent conditions, the saturated area of the Coalburn catchment increases (especially the mires-floodplains) and may even produce saturation excess runoff in areas. Wet deposition is likely to be rapidly transported to the drainage ditches and the catchment outfall . If this process is operating then there may be a sharp increase in sea-salts in the stream and dilution of catchment-derived inputs; this will be examined later in Chapter 5.

There is a significant positive correlation between chloride concentrations in the rainfall and stream ($p < 0.001$). This can be explained by the link between rainfall and the stream chemistry described above. Given that the wet deposition sample reflects the bulk rainfall chemistry over the previous period (approximately two weeks) it is not surprising that the river chemistry reflects the deposition signature for unreactive solutes such as chloride (i.e. the correlation include the necessary lag factor for residence time in the catchment).

Examination of the other chemical solutes revealed that rainfall and stream conductivity time series exhibit a similar relationship between the rainfall and stream chemistry. However, this correlation is weaker than the chloride signal and involves a time lag (Figure 3.8). However, visually the evidence suggests that there is a relationship between conductivity in the rainfall and stream (under certain conditions) and this will be examined in more detail in the following chapters. Examples where elevated rainfall and stream conductivity coincide include 01 August 1995; 14 February 1996; 01 August 1997 and 01 May 1997.

In terms of catchment processes, there would appear to be a complex linkage between rainfall and stream chemistry at Coalburn. During extreme hydrological events, the rainfall may affect the stream chemistry for unreactive solutes and conductivity; however, for reactive solutes such as pH the catchment process and gradients dominate the catchment response. During less extreme events there appears to be a lag between the rainfall and stream chemistry for unreactive solutes (and conductivity) as indicated by their similar seasonal patterns. These patterns sit nicely with the ‘reservoir’ concept presented by (Robson, 1993), whereby the ‘event’ water does not generally contribute during the initial catchment response but enters the catchment chemical reservoir. The chemical reservoir then affects succeeding events, although this component will be subject to dilution and alteration by subsequent deposition.

This serves to demonstrate the event intensity, flow source, reservoirs, residence times and pathways are critical factors in controlling the catchment response. Furthermore, the linkage between rainfall and stream chemistry implies the pollution climatology and catchment conditioning are likely to be important in determining the stream hydrochemical response during and following an event (i.e. acid deposition and sea-salt events may be important).

3.5.1.2 Weathering and Inorganic Leaching Component

Calcium and magnesium have maximum concentrations under base-flow conditions and are derived from weathering reactions in the deep soil-water and shallow groundwater that has a long residence time (Hind, 1992; Robinson et al., 1998). The concentrations of calcium and magnesium rapidly decline as flows increase reflecting the dilution of the deep-water by base cation depleted soil water. At flows greater than 20 ls^{-1} the concentrations remain approximately constant. The rapid decrease reflects the distinct vertical gradients observed in the soil profiles at Coalburn (Hind, 1992; Robinson et al., 1998) and, to some extent, the importance of the peaty-gley areas as a source of these solutes. The peaty-gley sub-catchment, while only being a small percentage of the whole catchment is located on the steep slopes closer to the catchment outfall, and water from this area is likely to be displaced during the early part of an event. At higher flows, the calcium and magnesium concentrations remain constant, which suggests that deep-water pathways contributions continue and that a new equilibrium state is reached. The magnesium pattern is slightly more complex as it may exhibit a composite response. During low flow, it is derived from weathering, while at high flows a component may also be derived from the marine inputs of rainfall that can affect the stream chemistry as detailed above.

Aluminium has its lowest concentrations during base-flow conditions. The aluminium concentrations rapidly increase with flow, although the relationship shows a degree of scatter reflecting the variability of the water sources and pathways during an event. At higher flows aluminium concentrations show evidence of decreasing. These characteristics reflect the catchment soil and geology. The upper soils/peat are acidic at Coalburn and this will mobilise the large aluminium pool available in the upper soil (Hind, 1992; Baglee, 1994), through the breakdown of oxides and hydroxides within the acidic soil zones (Neal et al., 1992). Under base-flow conditions the streamflow is derived from the deep-water component that is well buffered and any aluminium that has migrated from the acidic soil horizons will be precipitated. During high-flow events, the streamflow is increasingly derived from the upper soil-water component resulting in a gradual and continuous increase in aluminium concentrations. With intense or long duration storms, there may be infiltration or saturation excess that results in a component of the rainfall signal reaching the stream and diluting the soil derived solutes, such as aluminium; observed for streams in the Llyn Brianne by Soulsby (1995b). This adds further weight to the hypothesis that the rainfall signal effects the stream chemistry under certain conditions. Alternatively, it could reflect that the upper soil profile is depleted in aluminium (Neal et al., 1992).

Coalburn soils have a large pool of weatherable iron and, in some locations, it exhibits a pattern of increasing concentration in soil water with depth (Hind, 1992). Coalburn stream exhibits its highest iron concentrations at low flow and, as flow increases to greater than 10 ls^{-1}, concentrations decrease in an exponential manner due to dilution. This may reflect the behaviour of iron in the environment; the mobility of iron not only being a function of pH but also the redox conditions; as a result it is not necessarily precipitated at high pH (O'Neill, 1993). There are two hypotheses that could explain the patterns observed at Coalburn:

- Firstly, under base-flow the iron could be derived from a deepwater/ground component, at depth reducing conditions may mobilise iron (II) from the boulder clay/sandstone geology (Neal et al., 1986). However, when this water discharges to the stream the iron (II) would be expected to oxidise and precipitate to form ochreous deposits. Ochreous deposits (orange staining and black gelatinous deposits) have been observed on the bank sides at Coalburn where the baseflow seeps to the stream. These deposits may be dissolved into the water or complexed by the organic species that present in the Coalburn stream (O'Neill, 1993).

- Alternatively, under base-flow conditions, the peat sub-catchment still contributes a significant component of the catchment flow. In these areas, the pH remains low and reducing conditions exist, mobilising iron that will then be organically complexed (i.e. does not precipitate). The limited spatial surveys carried out as part of this study and Hind (1992) show that during base-flow conditions the highest concentrations of iron are observed in the peat sub-catchment. Given the explanation it may be expected that the aluminium concentrations would increase; however, the spatial surveys indicate the pH is to high and the aluminium would precipitate (note aluminium is not sensitive to redox conditions).

The causal mechanism of the observed response could result from either one or a combination of these hypotheses, especially as there is a positive relationship between DOC and iron concentrations. To determine the exact cause of this response would require further fieldwork and this could be a focus for future studies.

The pattern for manganese is more complex and would appear to be a composite of iron and aluminium. At extremely low flows ($< 5\ ls^{-1}$) the concentrations begin to increase slightly as manganese is also affected by redox reactions and will act in the same manner as iron. As flow increases the concentrations decrease slightly, however, as flows continue to increase there is a small increase in manganese, although there is large degree of scatter in this pattern. Manganese is also derived from the breakdown of oxides and hydroxides within the acidic soil zones and during hydrological events the streamflow is increasingly derived from the upper soil-water component resulting in an elevated concentrations.

Sulphate exhibits a slight increase in concentrations with flow, this implies that mineral acidity could play an important role as a source of acidity during events.

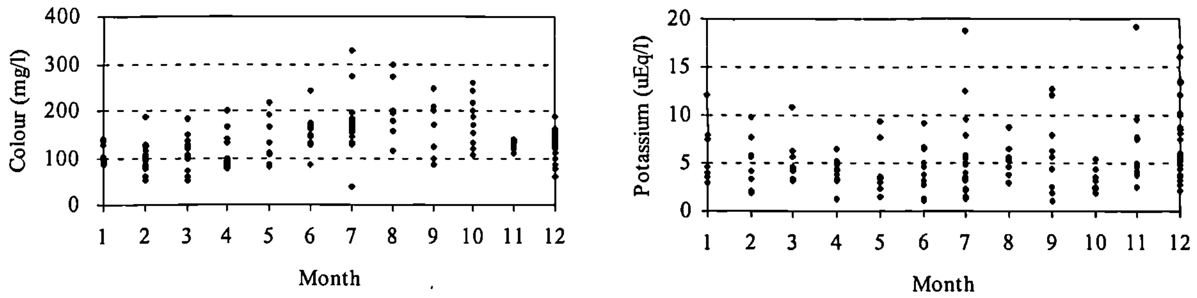
3.5.1.3 Nutrient and Biological Mediated Component

The nutrient and biologically mediated components include ammonium, nitrate and potassium, these are all biologically active in the nutrient cycle between the forest and soil ecosystem. These solutes show seasonal trends in their time series, the phases of which vary between solutes and may change from year to year for any one solute reflecting the variability in climate, flow paths and biological processes (Neal, et al., 1992).

At Coalburn, there is only a short time series available for the nutrients. The typical seasonal patterns for nitrate and potassium of leaching during winter (i.e. limited nutrient uptake by the forest) and retention during the growing season (i.e. summer) are indistinct. The low concentration of nutrients observed in the stream probably reflects the nutrient limited environment, and comparing the concentrations in the rainfall and river (Table 3.1 and 3.11) it is evident that the nutrients are being retained within the catchment. Furthermore, the nutrient solutes are close to their limit of detection leading to missing values, which make it more difficult to assess the trends. The nitrogen measured does not include the dissolved organic nitrogen component, which can be important where peat is present in the catchment.

The second group of biologically mediated solutes include total and dissolved organic carbon and colour. These solutes have temperature induced seasonal trends reflecting the microbial decomposition of organic matter in peat soils. For Coalburn, the streamwater concentrations of these constituents are at the lowest in winter and spring when the soils are cool wet and microbial activity is at a minimum (Figure 3.9). Concentrations then rise to a maximum towards the end of summer and into autumn, as warmer dryer conditions accelerates the breakdown of organic matter into a mobile form that leaches to the stream (Figure 3.9). While only a relatively short time series of dissolved organic carbon and colour are available, they show a slight increase throughout the years (Figure 3.9). This may reflect the weather patterns (especially the 1995 drought) or it may be indicative of the long-term trend to increasing DOC concentrations as observed by Reynolds et al. (1997) for the Plynlimon streams.

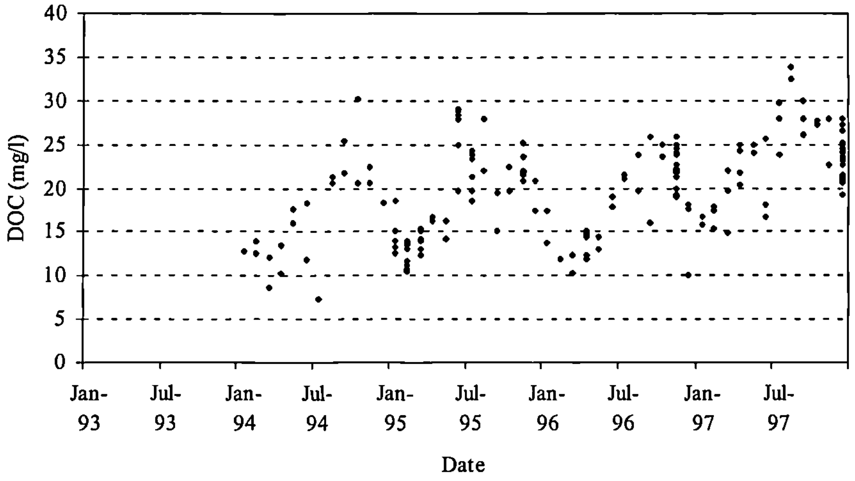
Figure 3.9 Patterns in biologically mediated solutes



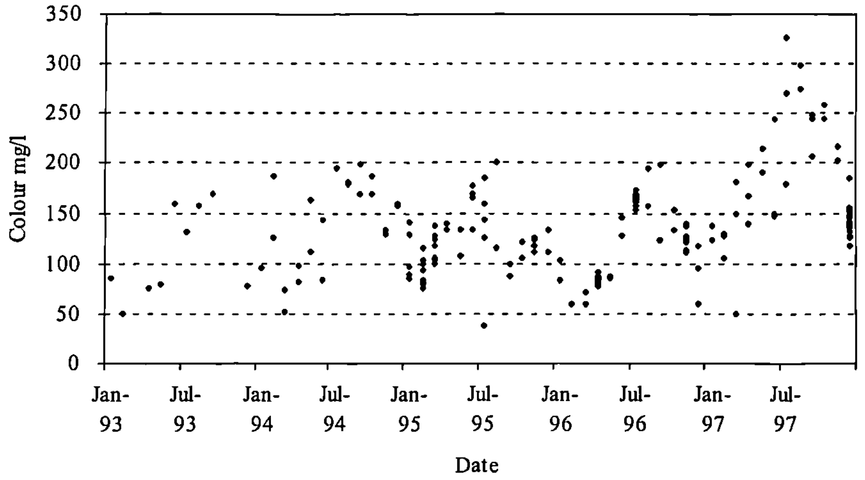
Colour

Potassium

Dissolved organic carbon times series



Colour time series



Dissolved organic carbon (DOC) and total organic carbon (TOC) do not exhibit the positive relationship with flow as observed in other studies and ascribed to an increasing flow component from the soil zones (Neal et al., 1997a; Jenkins et al., 1990; Robson, 1993). The lack of correlation at Coalburn may result from the importance of the peat as a flow source area during low flow periods and the seasonality in DOC concentrations (i.e. highest in late summer when flows are likely to be low). Consequently, high DOC values can be observed during periods of low flow as well as during high-flows when soil and peat sub-catchment water dominates.

3.5.2 Spatial variability of streamflow in the Coalburn catchment

Previous studies have sampled the spatial variations in surface water quality in the catchment (Robinson & Hind, 1991; Hind, 1992; Mounsey and Newson, 1995) and the findings are summarised in Robinson et al. (1998):

> *"To the eastern side of the main stream, waters are characterised by high values of pH, conductivity and concentrations of sodium and calcium; there is no coloration of these waters. To the western-side waters are the converse of this."*

This broadly reflects the distribution of soils in the catchment, with the peaty-gley on the eastern side, while the remainder of the catchment is covered by deep peat (Figure 2.2).

To confirm these patterns and understand the role of different sub-catchments in generating the stream water chemistry under storm and base-flow conditions, a spatial survey of the catchment water quality was undertaken (Figure 2.1). The sampling strategy included the main tributaries of Coalburn on the different soil types and was a sub-set of the sample points used by Hind (1992) for continuity of the data series. The Environment Agency carried out eight surveys of these sites and the samples were analysed for the full suite of determinands (Table 3.13 & 6.2). Newcastle University surveyed these sites more regularly (in total 29 times) and these samples were analysed for pH, conductivity and alkalinity (Figures 3.10 and 3.11 and Table 6.2).

Figure 3.10 Conductivity spatial variability – Newcastle Data

```
                                 Individual 95% CI
Sample date     Mean   -+---------+---------+---------+---------+
17/06/97        60.4            (----*----)
01/07/97        53.9        (----*----)
17/07/97        63.4              (----*----)
22/09/97        77.6                        (----*----)
13/10/97        72.1                    (----*----)
27/10/97        90.1                                (----*----)
06/11/97        84.8                             (----*----)
20/11/97        70.6                   (----*----)
10/12/97        91.2                                 (----*----)
15/01/98        75.0                      (----*----)
29/01/98        77.4                        (----*----)
12/02/98        82.4                           (----*----)
26/02/98        79.8                         (----*----)
11/03/98        69.3                  (----*----)
24/04/98        65.3                (----*----)
13/05/98        66.0                (----*----)
11/06/98        55.9         (----*----)
26/06/98        67.0                 (----*----)
27/08/98        55.8         (----*----)
09/09/98        51.8       (----*----)
                       -+---------+---------+---------+---------+
                     45.0      60.0      75.0      90.0     105.0

                       Individual 95% CI
Site            Mean   ----+---------+---------+---------+-------
SM DS 5         60.6   (---*----)
SM1             62.6     (---*---)
SM10            65.6       (----*---)
SM12            68.3          (---*---)
SM13            61.8    (---*----)
SM2             76.5                 (---*---)
SM5             93.0                              (---*----)
SM7             61.6    (---*----)
SM8             84.6                       (---*----)
                       ----+---------+---------+---------+-------
                        60.0      72.0      84.0      96.0
```

Figure 3.11 pH spatial variability – Newcastle Data

```
                       Individual 95% CI
Sample date     Mean   --------+---------+---------+---------+---
17/06/97        5.50                           (--*--)
01/07/97        4.52              (---*--)
17/07/97        6.00                                 (--*--)
22/09/97        6.12                                  (---*--)
13/10/97        5.59                            (--*--)
27/10/97        6.30                                     (--*--)
06/11/97        6.44                                      (---*--)
20/11/97        5.69                             (--*--)
10/12/97        3.67    (--*--)
15/01/98        3.78     (--*--)
29/01/98        4.72                 (--*--)
12/02/98        4.30            (--*--)
26/02/98        5.01                    (---*--)
11/03/98        3.79     (--*---)
24/04/98        4.38            (---*--)
13/05/98        4.34            (--*---)
11/06/98        3.76     (--*--)
26/06/98        4.96                    (--*--)
06/08/98        3.83      (--*--)
27/08/98        4.46             (---*--)
09/09/98        4.61               (---*--)
                       --------+---------+---------+---------+---
                            4.00      4.80      5.60      6.40
```

```
                       Individual 95% CI
Site            Mean   --+---------+---------+---------+---------
SM DS 5        4.959                       (--*-)
SM1            4.944                       (--*-)
SM10           4.895                       (-*-)
SM12           4.357               (-*--)
SM13           5.068                         (-*--)
SM2            5.649                                 (--*-)
SM5            6.100                                        (-*--)
SM7            4.405                (-*-)
SM8            3.542   (--*-)
                       --+---------+---------+---------+---------
                     3.500     4.200     4.900     5.600
```

Both surveys were randomised block survey and a one-way anova test to assess the observed differences is not applicable as the variation could come from the between and/or within site variation (Moore and Cobby, 1998). A two-way anova test was applied to the Newcastle University pH and conductivity data (Figures 3.10 and 3.11). The results indicate that there are indicate there are significant differences ($p < 0.001$) in the stream pH and conductivity in terms of both spatial and temporal variability across the catchment.

The pH (and alkalinity) values are significantly higher on the eastern peat-gley sites (SM5 and SM2) than those on the deep peat sub-catchment (SM8, SM12 and SM7). During low flows some of the sites on the peat sub-catchment (SM 7, 10 and 12) exhibited elevated pH values, given the presence of peat. Cryer (1978) (in Robson, 1993) sampled peat waters in the pH range 6-7 for a catchment near Plynlimon and Robson (1993) also observed well-buffered waters at depth in the peat of the Afon Gwy catchment. These observations were ascribed to a process of upward filtration of mineral rich waters from beneath the peat that elevated the pH and mineral status of the waters from these sites. A similar mechanism could be effecting the Coalburn catchment during base-flow periods, but requires further investigation to confirm. Site SM8 remained acidic through out the surveys (even during base-flow conditions) varying from pH 4.80 to 3.10. The SM8 tributary is relatively large joins the main channel slightly upstream of the catchment outfall; however, samples taken at the catchment outfall indicate the main stream buffers this input before it reaches the catchment outfall.

The conductivity values are significantly higher on the eastern peat-gley sub-catchment (SM2 & SM5) and on the peat sub-catchment at SM8. The high conductivity at the peaty-gley sites can be attributed to high concentrations of weathered/dissolved solutes with the drainage from these sites reflecting the mineral nature of the soils. The high conductivity at SM8 reflects the low pH and, a significant component of the conductivity will be derived from hydrogen ions and aluminium species. Consequently, an increase in the conductivity at the catchment outfall could represent an increased contribution from one or both of these areas.

For the Environment Agency data, missing data precluded two-way anova analysis. For this data the plots of the 95 percentile concentrations for the sites have been calculated and used to assess spatial patterns. If the 95 percentile confidence limits do not overlap a significant differences between the sites can be inferred ($p < 0.05$).

Colour and dissolved organic carbon stream water concentrations have a distinct spatial pattern with the eastern peaty-gley sub-catchment (SM2 and SM5) having significantly lower concentrations of these solutes compared to the peat sub-catchment sites. This reflects the mineral/organic status of each soil type. In contrast, the patterns for calcium have the highest concentrations on the peaty-gley sub-catchment; however, high concentrations of calcium have been observed at SM10/12 during low flow conditions, despite being located on the peat sub-catchment. This observation could be explained by the upwelling mechanism postulated above. There is a significant difference between the sites SM2 and SM8 in terms of the calcium concentrations.

Aluminium concentrations are generally higher on the peat sub-catchment resulting from the low pH encountered at these sites, however, SM2 on the eastern peat-gley showed one high aluminium concentration during the early part of an event. Iron concentrations are similar, being slightly higher on the peat sub-catchment sites. This lends support to the hypothesis that iron is derived from the peat sub-catchment during low flow periods, as discussed above.

These results corroborate and elucidate upon the previous findings, presenting a complex mosaic of within catchment variability for Coalburn water quality. Broadly, water chemistry reflects the variations in the soils and associated geochemical processes; the eastern peaty-gley soils can be characterised by high pH, conductivity and concentrations of magnesium and calcium; there is little coloration of these waters. Tributaries on the peat sub-catchment are the converse of this. However, there are anomalies, for example the higher pH and base cation concentrations at sites SM10 & 12 on the peat, that imply a broad classification cannot not fully encompass the variability or processes occurring in the catchment.

Table 3.13 Summary of Coalburn spatial variations in stream chemistry

	River	SM8	SM2	SM13	SM D/S 5	SM 5	SM 7	SM 12	SM 10
pH	4.47	3.92	6.44	7.15	5.4	6.96	4.4	4.25	4.69
Hydrogen	34.02	120.3	0.36	0.07	3.94	0.11	39.42	56.6	20.63
Al	6.5	9.9	9.9	3.6	4.8	4.8	5.2	6.7	5.1
Ca	186	130	471	696	286	641	224	401	402
Mg	60	43	73	151	119	88	96	120	114
Na	208	228	299	202	199	229	211	222	233
K	7.6	2.4	8.8	3.3	3.3	4.8	3.0	5.2	3.2
Cl	266	318	376	233	252	301	269	279	264
SO_4	215	158	212	127	103	178	122	131	120
NO_3	7.4	0.28	1.3	1.3	1.7	6.4	2.0	6.5	1.6
NH_4	2.6	1.6	0.9	1.6	1.7	1.3	2.5	6.6	2.2
DOC	18.5	23.8	13.3	23.3	22.9	13.7	23.9	21.1	21.1
TOC	21.7	24.1	13.2	23.1	23.0	13.8	24.0	21.1	21.1
Colour	112	160	65	215	204	97	187	156	174
Mn	1.0	ND	ND	0.7	0.5	0.7	0.5	0.8	0.6
Fe	9.8	15.1	9.7	19.2	17.3	8.2	17.0	14.8	22.9
Conductivity	61.9	84.8	90.4	9.9	80.9	124.2	78.9	95.4	76.2
SiO_2	1.9	ND	ND	ND	ND	ND	ND	ND	ND

Key

All values are flow weighted means.

Units All units are in μEql^{-1} except:

Al and Fe are in $\mu Moll^{-1}$; DOC, TOC, SiO_2 and Colour in mgl^{-1}

Conductivity in μScm^{-1}

ND – no data

The soil type distribution, relative dominance and the different chemical signatures are important controls of the Coalburn hydrochemistry. The peaty-gley soils are located near the catchment outfall and are generally on the steeper slopes, and by virtue of this will contribute during the early part of an event. In contrast, the peat soils are further away from the catchment outfall, are not as steep and are likely to contribute during the later phases of an event. The relative area each soil type covers in the catchment also requires consideration; the peaty-gley only covers approximately 25% of the catchment while the peat covers the remaining 75% (Robinson et al., 1998; Figure 2.2).

The contribution from the peaty-gley sub-catchment during the early phase of an event is likely to buffer the acidic signal from the peat and mitigate a rapid pH fall during an event. At some point in an event, there is likely to be a 'break point' or chemical change when the Coalburn chemistry changes from the peat-gley to peat dominated signal, reflecting the dominance of peat in the catchment. Despite the peat signal being dominant in the Coalburn catchment, it does not completely suppress the peaty-gley signal which plays an important role in ameliorating the acidity at the catchment outfall. If the catchment were all peat, or if/when the peaty-gley signal were reduced, the acidity would be greater. These factors are clearly demonstrated below and are returned to in later chapters.

On 01 July 1997 a catchment survey was carried out on the falling limb of a large event (Table 3.14). If the pH at the catchment outfall and SM8 are compared it is clear some buffering must be occurring. Similarly, for site SM5 (located on a stream draining from the peaty-gley), samples are taken upstream (SM7, mainly draining from the peat area) and downstream (SMD/S5) of its confluence with the main channel, and this is also clearly buffering the main channel. This would suggest that the peaty-gley sources had an ameliorating effect, even during the later stages of a large event when the peat signal is expected to dominate. On 27 March 1997 a catchment survey was carried out on the rising limb of a relatively small event and the buffering appears slightly greater, suggesting the amelioration is greater during the rising limb, as postulated earlier.

Table 3.14 Buffering in the Coalburn catchment

Site	01 July 1997	27 March 1997
Catchment outfall	4.50	4.89
SM8	3.90	3.97
SM7	4.10	4.36
SM5	5.70	6.94
SM D/S 5	5.30	4.73

pH in pH units

In summary, the Coalburn catchment has distinct spatial patterns and two chemical signatures have been identified from the peaty-gley and peat sub-catchments. The spatial distribution of the soils in terms of area and location has a fundamental influence on the volume and timings of the delivery of waters with different chemistries from these sub-catchments. The results have clearly demonstrated that the relatively small peaty-gley sub-catchment has a profound effect on the Coalburn chemistry and, therefore has important implications for the role of management to mitigate against adverse impacts of land use. Finally, the influence of the spatial signatures must be considered, along with the other factors, when interpreting of the casual mechanisms of events in later chapters.

3.5.3 Storm and base-flow characteristics.

At Coalburn the physical structure of the catchment combined with a variable input signal, result in an infinitely variable hydrochemical response. However, consistent patterns in the base and storm flow chemistries have emerged from the study.

A typical base-flow chemistry was determined from flows less than the 90 percentile mean daily flow (Table 3.11; Figure 3.6). This shows the Coalburn pH typically rises to well above seven as the shallow groundwater sources and throughflow from the deeper horizons dominate. Under these conditions weathering processes and long residence times enables the neutralisation of acidity within the soils and as a consequence metals such as aluminium are precipitated. As this water passes to the stream it degasses carbon dioxide to produce low acidity, base cation enriched (especially calcium and magnesium) and aluminium depleted base-flow chemistry (Figure 3.6) (Neal et al., 1992; Robson, 1993). During baseflow the bicarbonate component is a significant proportion of the total ionic charge, although this is reduced at high flows (Figure 3.6). Comparing the base-flow and storm flow signature using t-tests it was apparent that the base-flow had significantly ($p < 0.05$) higher values of pH, colour, conductivity, magnesium, calcium and iron concentrations.

Storm flow chemistry was determined from flows outside the v-notch at the main gauging weir, which was designed to contain the 98 percentile flow. The storm flow is acidic and this is likely to be due to the increasing volumes of water being derived from near surface flowpaths through organic peat horizons and the peat sub-catchment (Table 3.11; Figure 3.6). This water overwhelms the buffering capacity of the deep-water, dilutes base cation concentrations and decreases colour, whilst, aluminium and hydrogen ion concentrations increase. Comparing the storm-flow and base-flow, the storm-flow had significantly ($p < 0.05$) higher values for ammonia, nitrate and aluminium concentrations. During extreme hydrological events, there may be a slight recovery in the hydrogen and aluminium concentrations, suggesting either a component of rainwater is reaching the stream at such times and/or a 'washout' process occurs. A similar decrease in aluminium has been observed at Plynlimon by Neal et al. (1992) and was ascribed to lower aluminium concentration in the upper soil horizons, whereas Soulsby (1995b) explained this through a dilution effect from event water at Llyn Brianne.

Seasonal patterns have been observed and linked to the biological changes during the year at Coalburn. However, the distinct chemical signatures in the base and storm flows also introduce a flow related seasonality. This is due to the predominance of high flows during the winter period and the change in the relative proportions of soil and deepwater contributions to the stream. For example, calcium has its maximum concentrations during the summer period due to its association with the deep-water baseflow signal; whereas aluminium exhibits the reverse pattern as would be expected. Similar patterns have also been observed by Neal et al. (1992).

The results presented above are broadly consistent with the two component mixing regime. This was first proposed for the Hubbard Brook in the eastern USA (see Likens and Bormann, 1995), and later adopted by Neal et al. (1992) and Robson (1993) for British upland catchments with a substrate of high buffering capacity and organic rich peat surface horizons. However, the soil distribution and spatial variability of the water chemistry at Coalburn introduces a strong dynamic lateral variability into the catchment response. Consequently, the observed hydrochemical response at Coalburn will be a product of the dominant hydrological pathway(s) through the soil (vertical) and the main contributing area (lateral). The varying proportions of these chemically different waters may also change with antecedent conditions, event conditions and season.

3.6 The Coalburn catchment fluxes

3.6.1 Atmospheric flux

The total atmospheric flux entering the Coalburn catchment cannot be calculated, as the quantity of dry deposition is unknown, however, this section examines the wet and cloud mist deposition to the ecosystem.

The average annual flux from rainfall and cloud mist deposition were derived (Table 3.15). The rainfall component was calculated using the mean annual precipitation for Coalburn of 1350 mm (Robinson et al., 1998) and the volume weighted rainfall concentrations for the study. Two values for cloud mist flux were determined, both used the geo-mean cloud mist concentrations for the study, and cloud mist depths of 50mm and 90mm were used to reflect the range quoted by Robinson et al. (1998). The atmospheric flux represents the sum of rain and cloud deposition (Table 3.15).

Despite the relatively small input of cloud mist to the wet deposition volumes (50 mm - 3.7% and 90mm - 6.7%), the high concentrations observed makes it an important component of the wet deposition flux. For the 90mm input the cloud mist is estimated, on average, to contribute 40% of the atmospheric flux, although this varies for individual solutes, ranging from 62% (Na) to 12% (NO_2). The flux and range is slightly less when 50 mm is considered with an average contribution of 28% to the atmospheric flux and ranging from 48% (Na) to 7% (NO_2).

Robinson et al. (1998) stressed the Coalburn cloud mist volumes are only preliminary and are likely to be over-estimates. This health warning on the volumes of cloud mist has implications on the estimates of wet deposition flux to the Coalburn catchment (Table 3.15). However, the high concentrations observed in the cloud mist implies the cloud mist flux is not very sensitive to small changes in volumes. For example, if the cloud mist figures were drastically reduced to 25mm (1.85% of water balance) the cloud mist component would still represents 17% of the atmospheric flux, and an important pathway of solutes into the Coalburn ecosystem.

Table 3.15 Wet deposition flux at Coalburn

	Cloud Mist Geo-mean	Rainfall VW Mean	E Ratio	Rainfall Flux 1350mm	Cloud Mist 50 mm			Cloud Mist 90 mm			Cloud Mist 25 mm		
					Cloud mist flux	Total wet dep'n	% Cloud mist	Cloud mist flux	Total deposition	% Cloud mist	Cloud mist flux	Total dep'n	% Cloud mist
Al	8.7	0.9	10.2	0.3	0.1	0.4	27.5	0.2	0.5	40.6	0.1	0.4	15.9
Ca	308.0	25.4	12.1	6.9	3.1	10.0	31.0	5.6	12.4	44.7	1.5	8.4	18.3
Mg	569.0	26.8	21.2	4.4	3.4	7.8	44.0	6.2	10.5	58.6	1.7	6.1	28.2
Na	2389.0	97.9	24.4	30.4	27.5	57.8	47.5	49.4	79.8	61.9	13.7	44.1	31.1
K	70.0	7.8	9.0	4.1	1.4	5.5	24.9	2.5	6.6	37.4	0.7	4.8	14.2
Cl	2687.0	144.5	18.6	69.2	47.6	116.8	40.8	85.7	154.9	55.3	23.8	93.0	25.6
SO_4	641.0	51.5	12.4	33.4	15.4	48.8	31.6	27.7	61.1	45.3	7.7	41.1	18.7
NO_3	520.8	26.4	19.7	22.1	16.1	38.2	42.2	29.1	51.1	56.8	8.1	30.1	26.8
NO_2	1.0	0.5	2.0	0.3	0.0	0.3	6.9	0.0	0.4	11.8	0.0	0.3	3.6
NH_4	362.7	33.4	10.9	8.1	3.3	11.4	28.7	5.9	14.0	42.0	1.6	9.8	16.7
DOC	4.9	2.1	2.3	28.4	2.5	30.8	8.0	4.4	32.8	13.5	1.2	29.6	4.1
TOC	5.0	1.5	3.4	19.7	2.5	22.2	11.3	4.5	24.2	18.6	1.3	21.0	6.0
Mn	1.5	0.6	2.6	0.2	0.0	0.2	8.9	0.0	0.2	14.9	0.0	0.2	4.6
Fe	7.7	0.5	15.7	0.4	0.2	0.6	36.8	0.4	0.8	51.2	0.1	0.5	22.5
Mean			11.4				27.8			39.5			16.9

Key

Units Cloud mist geomean and rainfall volume weighted mean units are in μEql^{-1} except: Al and Fe are in $\mu Moll^{-1}$; DOC, TOC, in mgl^{-1}

E Ratio – ratio of the geomean cloud mist and volume weighted rainfall to give enrichment ratio E.

Flux and Total Deposition Flux kg ha^{-1} yr^{-1}

One important characteristic of cloud mist deposition is that it has never been recorded as exceeding the forest storage capacity (Robinson et al., 1998). Consequently, the cloud mist deposits must remain in the canopy until the next rainfall event, this catchment conditioning process will be in addition to that by dry deposition and may be an important factor in explaining the catchment responses.

Similar wet deposition fluxes were calculated by Wilkinson et al. (1997) for Plynlimon using an average rainfall of 2459mm and a cloud mist input of 140mm. Even when the volumetric differences were taken into account it was evident that Coalburn receives a relatively high input of terrestrial ions and a lower flux of marine ions. This is confirmed by the comparison of rainfall component of the wet deposition flux with the rest of the UK (Table 3.16).

Table 3.16 Coalburn rainfall flux

Solute	Coalburn	UK Range
Non-marine sulphate	3.0	<0.3 to >1.2
Nitrate	3.4	<0.2 to >0.5
Ammonium	0.7	<0.2 to >0.6

Flux g m^{-2} yr^{-1}. Data from Neal et al. (1996).

3.6.2 Average catchment flux

The average catchment flux (Table 3.17) is the average river flux minus average wet deposition flux, and gives an indication of the flux derived from the catchment and dry deposition. The values were derived using the average rainfall (1350 mm) and cloud mist (67.5mm) deposition as volumes and volume weighted mean and geomean concentrations for rainfall and cloud mist respectively. The river flux was calculated from the average of the yearly total flows between 1994 to 1997 and the flow weighted mean concentration.

This method of calculating fluxes is crude but is only intended to illustrate the likely patterns and processes operating in the Coalburn catchment and is not an in depth analysis of catchment stores and fluxes. Furthermore, the missing chemical data, especially rainfall chemistry, implies flux analysis cannot be applied at a finer resolution.

The average catchment flux demonstrates that the solutes can be separated into two groups. The first group is those that are derived primarily from the catchment (and/or dry deposition) source and include aluminium, calcium, sulphate, dissolved organic carbon, total organic carbon and iron. The second group are those that are derived primarily in the rainfall and appear to be retained in the catchment and include magnesium, sodium, potassium, chloride, nitrate and ammonia.

The pattern and grouping of the average catchment flux are broadly consistent with the observation made for the chemical signatures in Coalburn. The magnesium pattern was slightly unexpected, however, this probably reflects that it can be derived as a weathering product and in the marine deposition component.

Table 3.17 Coalburn catchment flux

Solute	Rainfall Flux	Cloud Mist Flux	Total Wet Flux	River Flux	Catchment Flux (River – wet)	Catchment Flux as Percent
Al	46	24	70	208	138	66
Ca	1032	625	1657	4428	2771	63
Mg	656	695	1351	860	-491	-57
Na	4556	5561	10117	5681	-4436	-78
K	619	277	896	353	-543	-154
Cl	10375	9644	20019	11202	-8817	-79
SO_4	5009	3117	8126	12268	4142	34
NO_3	3311	3269	6580	544	-6035	-1109
NO_2	47	5	51	142	91	64
NH_4	1221	662	1883	396	-1487	-375
DOC	4253	496	4749	21978	17229	78
TOC	2957	506	3463	25780	22317	87
Mn	32	4	36	33	-3	-10
Fe	55	44	99	650	551	85

Units Kg yr^{-1}

3.7 Summary

This study has gathered a substantial water quality database, of varying resolutions, for most elements of the hydrological cycle at Coalburn. The Coalburn hydrochemistry exhibits distinct patterns and characteristics, these are considered with respect to the topics put forward for discussion at the beginning of the chapter.

The results are comparable and elaborate on previous studies.

The data are broadly similar to other Coalburn water quality studies (Hind, 1992; Baglee, 1994; Wake, 1994; Waterfall, 1994; George, 1995; Grundy, 1995; and Hughes, 1995). The wet deposition is the exception, with pH results from this study being greater than those observed previously at Coalburn and nearby at Eskdalemuir. This study used a sampling frequency of twice-monthly that would appear not capture the extreme events and smooth the rainfall chemistry compared to the weekly frequency used by the others. The same is likely to apply to the cloud mist data. Future improvements to the Coalburn study may include increasing the sampling frequency for these components.

The routine and event sampled steam water quality has gathered the longest series of water quality data for the Coalburn catchment. This includes a wide range of conditions from base to high flows and with different antecedent and event conditions. The extent and quality of the data collected has enabled a fuller picture of the Coalburn hydrochemistry to be characterised by this study.

The episodic acidification status of the Coalburn catchment can now be properly assessed.

The precipitation at Coalburn has a mean pH of 5.39 which is slightly acidic, however, its true acidity may be greater and this is masked by the sampling frequency. The concentrations of non-marine sulphate, nitrate and ammonia observed in the precipitation suggest Coalburn can receive moderate levels of acid deposition through the wet deposition pathway. Cloud mist is more acidic with a mean of pH 4.26, and exhibits elevated concentrations of acidic anions on occasions.

The flow weighted mean pH of Coalburn was 4.47, which is clearly acidic, however, this is biased by the over representation of event samples. A more detailed analysis of the acid episodes duration, frequency and magnitude is carried out in Chapter 4. A better assessment of acidification status is the Ferrier and Harriman (1990) definition. Using this definition Coalburn is a transitional site i.e. it has positive Acid Neutralising Capacity (ANC) at low flow and a negative ANC at high-flow but retains a fish and invertebrate population.

The data has shown there are three distinct sources of acidity in the Coalburn catchment that can be classified into:

1. Organic and humic acids derived from the peat and pine needle litter layer.
2. Mineral acids derived from wet, cloud mist and inferred dry deposition of non-marine sulphate, nitrate and ammonium. These are mainly linked to anthropogenic sources and are delivered to the Coalburn catchment when the pollution climatology or deposition is from the easterly sectors.
3. The rainfall, cloud mist and inferred dry deposition shows periods of increased sea-salt deposition that could be the precursor of a sea-salt acid event.

While each of the above are distinct sources, it is not possible to apportion the acidity observed in the Coalburn stream directly to each source as the catchment integrates them into a single response.

The data identify the important chemical signatures and hydrochemical variations in the Coalburn catchment.

The important chemical signatures and variations identified in the Coalburn catchment are summarised in Table 3.18.

Table 3.18 Chemical signatures in the Coalburn catchment

Solute	Source	Comments
pH Alkalinity	Catchment	The pH and alkalinity strongly replicate the gradients in the catchment soils and the source of the water (i.e. soil/deep or peat/peaty-gley water). Thus, pH is an indicator of the source of water in the catchment and it may be a useful tool in assessing the changes in water sources during events.
Chloride	Atmospheric (Marine)	Atmospheric tracer due to its conservative behaviour and shows seasonality according to the rainfall pattern.
Sodium	Atmospheric (Marine)	Re-active and mediated by the catchment processes. Not a good source indicator. The sodium to chloride ratio in the precipitation and cloud-mist approximates to sea-water. Deviation from this in the Coalburn stream during events may be indicative of sea-salt events or catchment retention.
Sulphate – non marine.	Atmospheric (Terrestrial)	Normally used as an indicator of the extent of acidification caused by atmospheric sulphur inputs. Winds from an easterly direction yields precipitation, cloud mist and inferred dry deposition with elevated concentrations of sulphate. The link between deposition and stream acidification is complex and mediated by catchment processes, which implies this is not a good tracer.
Nutrients ammonium nitrate	Mainly atmospheric (Terrestrial)	Nutrients observed in high concentrations in the rainfall and cloud mist, however, are rarely present in the streamwater in similar concentrations. This may be a function of the nutrient limited status of Coalburn implying they are retained. Furthermore, they are subject to fluctuating seasonal changes owing to biologically mediated processes. As such, nutrients are unsuitable as source indicators.
Calcium and magnesium	Catchment (Deepwater/ peaty-gley)	While present in precipitation and cloud-mist, these solutes are indicative a catchment pathway/sources, specifically water that originated from the deep-water pathway, where weathering dominates or the peaty-gley sub-catchment.
DOC, TOC and Colour	Catchment (Peat/soil water)	These solutes have temperature induced seasonal trends, with a maximum towards the end of summer and into autumn. The solutes are not correlated with flow and this is explained by the dominance of peat in the Coalburn catchment, which is an important water source during low and high flow. These can be used as a source indicator of peat waters; however, careful interpretation is required.
Aluminium	Catchment (peat/soil water)	Elevated aluminium concentrations are indicative of soil water derived from the upper horizons. In contrast, aluminium concentrations are depleted in deepwater.
Manganese	Catchment	Elevated manganese concentrations are indicative of soil water derived from the upper horizons. Intermediate flows the concentrations are at a minimum and at low flows, this begins to increase possible reflecting the importance of the peat contribution.
Iron	Catchment	Indicative of catchment sources.

The Coalburn streamwater chemistry exhibits consistent patterns in the base and storm flow chemistries. Base-flow chemistry has high pH and enriched base cation concentrations, while aluminium concentrations are depleted. In contrast, storm flow chemistry is acidified with dilution of the base cation concentrations and decreased colour, whilst, aluminium and hydrogen ion concentrations increase. During storm flow events the chloride and sodium component can increase reflecting the wet deposition component, this may be indicative of a 'sea-salt' mechanism (Langan, 1989) or a 'direct' influence of the rainfall. Sulphate, potassium and nitrate also increase during events and could be caused by catchment conditioning when the antecedent weather was from the easterly sector.

Spatial sampling of the Coalburn tributaries revealed a complex mosaic of within catchment variability of water quality. There are two distinct chemical signatures. The eastern peaty-gley soils are characterised by high pH, conductivity and concentrations of sodium, magnesium and calcium; there is little coloration of these waters. Tributaries on the peat soils are more acidified and exhibit low pH and high aluminium, sulphate, dissolved organic carbon and colour. The chemical signatures from each soil type and the soil distribution (in terms of area, proportion and location) influence the streamwater hydrochemistry observed at the catchment outfall. These must be considered when hypothesising the casual mechanisms of events in later chapters.

A link can be established between stream chemistry and climate and chemical signatures.

At Coalburn, it was possible for chloride and conductivity, to demonstrate the rainfall chemistry signal can modify the stream chemistry. The response was not a direct one and could only be observed following extreme deposition events (which were few given the sampling frequency smoothing effect). The time lag implies the rainfall chemistry has a role in modifying the catchment stores and the subsequent events stream chemistry, the effects becoming progressively more dilute with subsequent events. During extreme high flows, there was evidence that the rainfall signal may have a direct influence on stream chemistry.

Furthermore, the wind direction and proportion of time from that direction has a bearing upon the input of ions from the atmosphere at Coalburn. The study could only consider the precipitation and cloud mist deposition, however, it can be inferred that when wet deposition ceases, dry deposition of a similar chemical signature is likely to begin

The analysis revealed that when winds were from the easterly sector the 'terrestrial' chemical signature yielded precipitation/cloud mist that was more acidic and had higher concentrations of acid anions. In contrast, westerly 'marine' winds had a signature of high pH and elevated concentration of marine ions. Consequently, antecedent weather can have a bearing upon the acidity status of the inputs to Coalburn and with respect to conditioning the catchment.

These two factors imply the antecedent conditions (i.e. quantity and quality of the pre-event water); residence time of that water (i.e. time for modification) and event conditions are important in controlling the Coalburn catchment response.

The water quality data are examined in more detail in the following chapters to determine if the episodic nature can be wholly or partially explained by the pollution climatology.

The hydrochemical variations can be can be explained by a combination of the catchment structure, biological factors, pollution climatology, flowpath and antecedent conditions.

The Coalburn stream chemistry reflects the input quality, soil type, underlying geology and the chemical gradients. Variation in the water quality would appear to be accounted for by the physical attributes of the catchment, antecedent conditions, event conditions, hydrological pathways and residence times. Essentially, varying proportions of chemically different waters from these sources can be used to explain the observed catchment response at any one time. Superimposed onto this are the temporal variations that are driven by climate (e.g. difference in water table depths between winter and summer) and biological mediation (Table 3.18)

The Coalburn hydrochemistry is broadly consistent with the two component mixing regime first proposed for the Hubbard Brook in the eastern USA (see Likens and Bormann, 1995), and later adopted by Neal et al. (1992) and Robson (1993) for British upland catchments with a substrate of high buffering capacity and organic rich peat surface horizons. However, the soil distribution and spatial variability of the water chemistry at Coalburn introduces a dynamic lateral variability. Consequently, the hydrochemical response at Coalburn will be a product of the dominant hydrological pathway(s) through the soil (vertical pathways) and the main contributing area (lateral pathway).

4 Coalburn: Short term dynamics in hydrochemistry.

Overview

The Coalburn catchment has a transitional acidity status with positive ANC during base-flow and negative ANC during high-flow. In transitional catchments, acid episodes occur with irregular frequency and knowledge of the duration, frequency and magnitude of the episodes is critical if the relationship between water quality and impact (e.g. fish survival) are to be understood. These aspects of hydrochemistry need to be adequately quantified to manage sensitive sites where there may be no biological signs of acidification; however, acid events may occur and the site may be sensitive to change.

Coalburn streamwater sampling data revealed the occurrence of acid episodes during runoff events, also the broad hydrochemical variations and chemical signatures. However, the sample data are a limited population and an 'appropriate' statistical technique would normally be used to predict the extreme water quality. However, the choice of an appropriate technique is not easy (Robson, 1993). Furthermore, spot sample data cannot elucidate the short-term variations, duration, frequency, and timing of hydrochemical events, all of which are important to the assessment of impact. At Coalburn the spot sample data have been supplemented by continuous pH, conductivity and temperature data, allowing a more detailed analysis of the short-term catchment-scale dynamics. The sampled and continuous data are utilised in this chapter to:

- *Assess the episodic acidification status of the Coalburn catchment and determine the magnitude, duration and frequency of the acid events.*
- *Identify the important short-term chemical signatures and variations in the Coalburn catchment and determine their value in conceptualising the processes underlying the acid episodes.*

4.1 Continuous data measurements at Coalburn

Prior to examining the continuous data, it is worth re-emphasising the inaccuracies that can exist in continuous field data (Chapter 2). The continuous pH time series has been corrected to improve its quality, however, on average errors of ± 0.2 pH units still exist. In contrast, the errors in continuous conductivity were not consistent and a generic correction could not be applied for long periods. For events, a conductivity correction has been applied where sampled and continuous data were available. When considering the catchment scale response, data accuracy is not the absolute limiting factor; the time series and direction of change can provide valuable information. The current accuracy of continuous measurements limits the subsequent analysis that can be applied and full use needs to be made of the spot samples. It would be unwise to apply trend analysis or rigorously compare the characteristics of events (e.g. rates of change) for continuous data, as the errors are of a similar magnitude to the expected observations.

The weir pool effect arises from the continuous monitoring occurring in the weir pool and the routine sampling being taken from the 'natural' channel upstream (Chapter 2). The correction of the continuous pH data will account for this factor. However, this was not possible for the conductivity data. During low flows, the sampled conductivity data were higher than the conductivity measured in the weir pool (Chapter 2); however, at high flows this difference diminished. These effects need to be borne in mind when analysing the data.

At Coalburn pH, conductivity and temperature values were logged on a fifteen-minute basis producing 96 values per day and 35 040 values per year, which is a substantial data set requiring considerable resource to analyse fully. Robson (1993) examined the effect of the time interval of continuous data with respect to characterising short-term dynamic variations. Robson (1993) concluded that a minimum of three hourly sampling was required, however, the resolution was substantially improved by hourly data; increasing the frequency to fifteen minutes did not produce an improvement in resolution. A similar exercise was carried out for the Coalburn data and the same pattern observed, consequently hourly continuous data have been used in the subsequent analysis. This is the best balance between data resolution and manageability.

4.2 Acid episodes in the Coalburn catchment

Episodic acidification was susinctly defined by Davies et al. (1992) as:

> ***'The process by which lakes and streams experience a short-term decrease of ANC, usually during hydrological events (transient increases in discharge) and over timescales of hours to weeks. An episode, then, is any short-term decrease of ANC and an acidic episode is an episode in which ANC falls below zero.'***

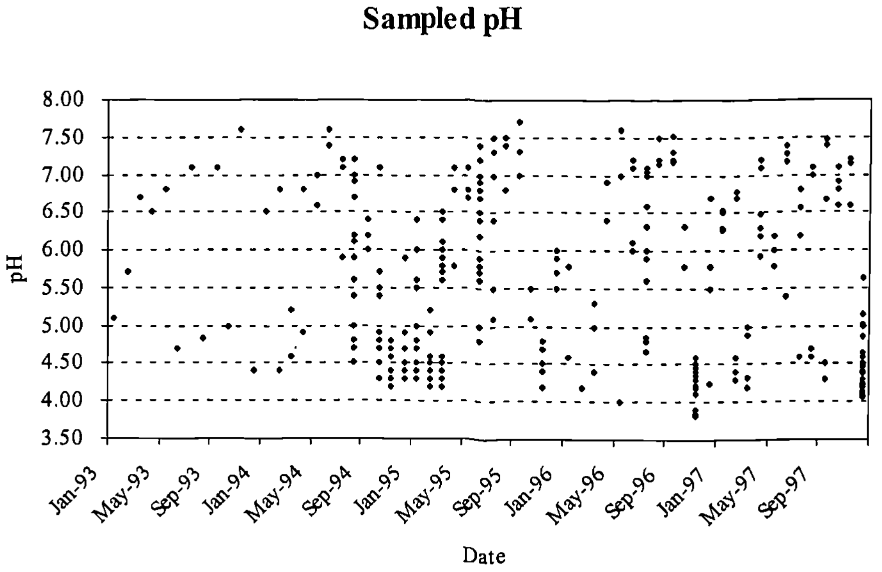
The continuous pH (pH_c) and ANC (see Chapter 6) time series clearly displays acid episodes, as defined above, and supports the previous observations of Hind (1992) and Robinson et al. (1994). The most striking feature of the pH_c times series for Coalburn is its range and dynamic nature (Figure 4.1), that has only become apparent using a combination of sample and continuous data gathered for this thesis. The sample data confirmed that Coalburn streamwater exhibits acute acidic episodes (pH min 3.3), while the continuous data revealed that acid episodes are associated with most hydrological events (Figure 4.1; Mounsey & Newson, 1995).

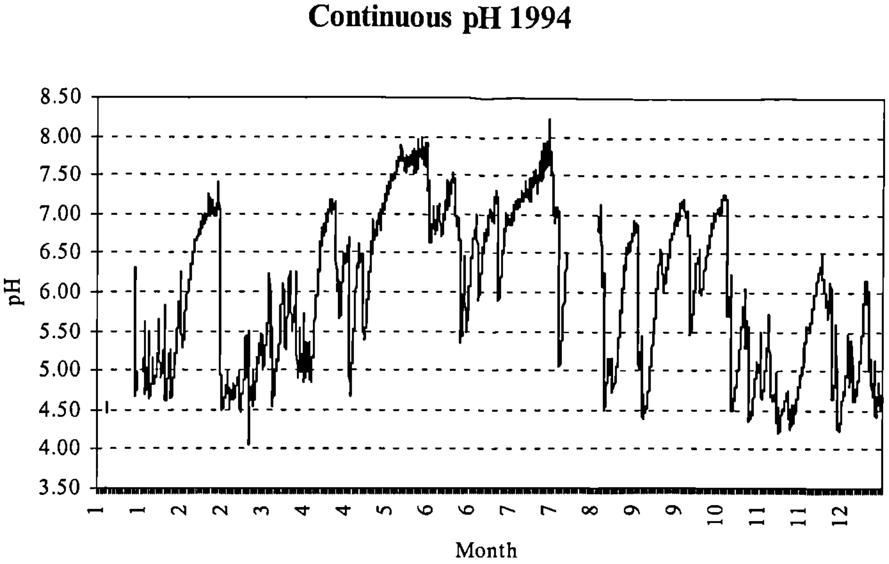
The duration, frequency and intensity of acid episodes are important factors in determining their impact. It is perhaps worth defining what these mean:

Duration	The length of time Coalburn is acidic or below a threshold.
Frequency	The frequency of acidic conditions or conditions below a threshold.
Magnitude	The degree to which Coalburn is acidified, this is best judged against an environment quality standard (water quality) or indicator species (biological).

The **duration** of acid conditions at Coalburn has been summarised using a pH_c duration curve (and histogram) derived from the hourly data (Figure 4.2). The pH_c indicates that Coalburn is acidic (i.e. $pH < 5.5$) for 39% of the time and is very acidic ($pH < 4.5$) for 8.5% of the time. The interpolated pH_c 95 percentile is 4.40, which compares with 4.20 from the sample data. The lower sampled pH 95 percentile only reflects the sampled data are skewed by event sampling that over-represents the high flow signature.

Figure 4.1 Coalburn pH times series





The pH duration has also been summarised using a histogram, derived from the hourly data (Figure 4.2). The histogram of pH_c exhibits a double maxima between 4.75-5.00 and 7.00-7.25 (Figure 4.2). This is likely to result from the catchment structure and seasonal variation in the water tables. During winter months the catchment gradually becomes saturated and an increasing amount of water is derived via shallow flowpaths through the more acidic soil horizons producing the lower maxima. In contrast, the summer low flows are associated with well-buffered deep throughflow and shallow groundwater producing the higher maxima. Robson (1993) observed similar distributions for the Plynlimon catchments. This distribution (chemical signature) is broadly consistent with the chemical gradients in the catchment and seasonal patterns observed in the sampled pH, calcium and magnesium that reflected the change in dominant flowpaths during summer and winter.

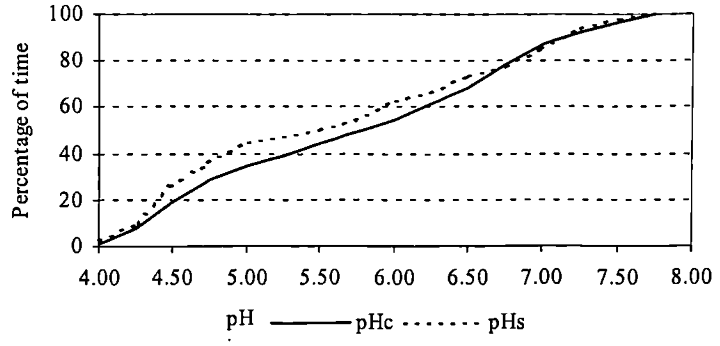
The **frequency** of acid episodes at Coalburn during the years 1994 to 1997 is summarised in Figure 4.2. For acidic conditions, pH < 5.5, Coalburn had a total of 95 events between 1994 and 1997. This frequency initially appears low, however, if the duration of the events is considered it is apparent that events with pH < 5.5 lasted for extended periods (up to 757 hours, 31.5 days). The low frequency of pH < 5.5 episodes is linked to the peat soils in the Coalburn catchment: during an acid episode the peat soils contribution rapidly and depresses the pH below pH 5.5, however, their low hydraulic conductivity results in a slow recovery extending the duration of the event.

If the threshold for pH is decreased to 5.0 and 4.5 the frequency of events during 1994 to 1997 was 120 and 119 respectively (Figure 4.2), and while the events were more frequent the duration was shorter. Nevertheless, this clearly demonstrates that acid episodes with pH less than 4.5 occur frequently at Coalburn and can last for long periods.

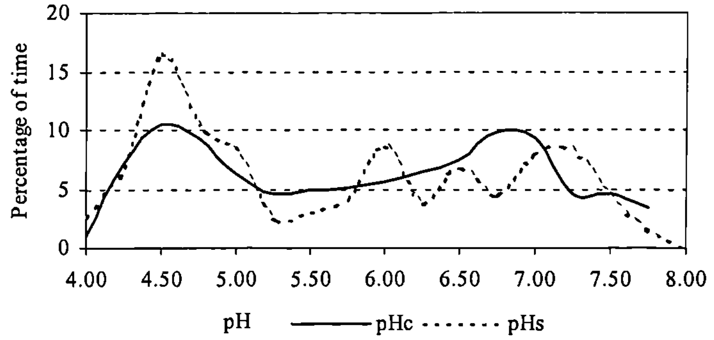
The **magnitude** is the degree to which Coalburn is acidified and is best judged against a standard or indicator. Several environmental quality standards exist for pH and Coalburn stream water quality has been assessed against these (Table 4.1). Coalburn streamwater would not meet the Freshwater Fish Directive (78/659/EEC) or Surface Water Abstraction Directive (75/440/EEC) standards; this has important implications for water quality planning and integrated river basin management (Chapter 7).

Figure 4.2 Coalburn pH duration and frequency curves

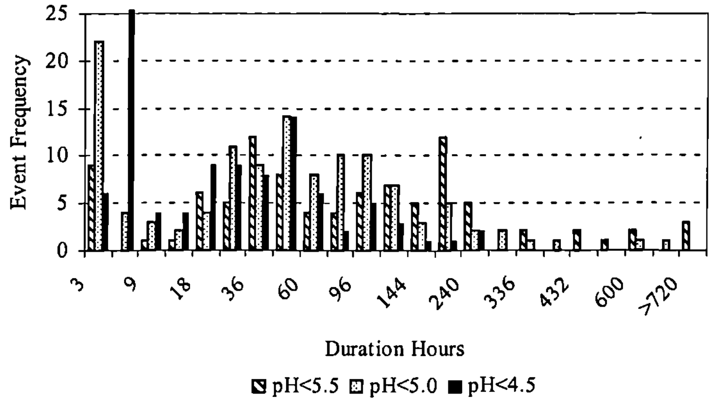
Coalburn pH duration curve



Coalburn pH duration



Coalburn acid event frequency



Coalburn acid event frequency

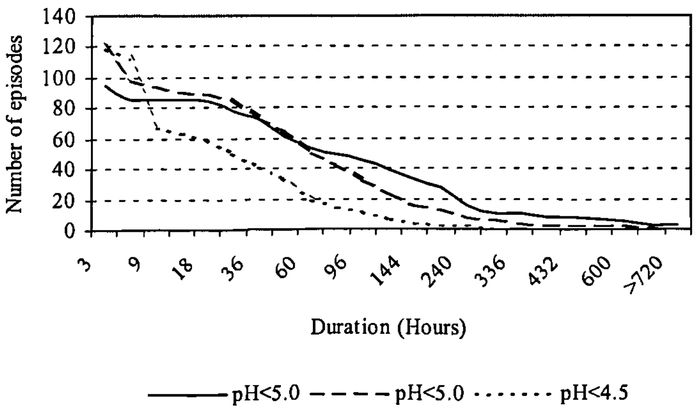


Table 4.1 Coalburn compliance against water quality standards

Legislation	Environment Quality Standard	Coalburn Compliance
EC Freshwater Fish Directive (78/659/EEC)	pH 6-9 (95 percent of annual samples should comply)	Coalburn is unlikely to comply being in this range for only 51 % of the time.
SWAD (75/440/EEC)		
Treatment A1	pH 6.5-8.5	Coalburn is unlikely to comply and is only in this range 51 % of the time
Treatment A2 and A3	pH 6.5-9.0 (90 percentiles)	
Treatment A1	Dissolved Fe – 0.3mgl^{-1}	Fail as 95 percentile 1.34 mgl^{-1}
Treatment A2	Dissolved Fe – 2.0 mgl^{-1}	Pass as 95 percentile 1.34 mgl^{-1}
Treatment A3	Dissolved Fe – 1.0 mgl^{-1} (95 percentile)	Fail as 95 percentile 1.34 mgl^{-1}
Protection of freshwater fish (UK EQS –Mance and Campbell, 1988)	Total Fe - 2.0 mgl^{-1} (Annual average)	Pass as annual average 0.7 mgl^{-1}

To assess the importance of acid episodes and the impact on survival of fish and other biota the important chemical variables have been identified as pH, calcium and aluminium with the following critical thresholds:

pH	< 5.50.
Calcium	< 50 μEql^{-1}
Filtered aluminium	> 50 – 80 μgl^{-1}

Sources: Brown (1983), Harriman et al. (1990) and Ormerod et al. (1989).

However, the intrinsic difficulties in relating a concentration to effect should be remembered when considering these absolute figures (Gee and Jones, 1997).

At the catchment outfall, Coalburn exceeds the pH threshold for 39% of the time (using pH_c). The minimum recorded calcium concentration is 88 μEql^{-1} and, even during extreme hydrological events the calcium concentration remains above the 50 μEql^{-1} threshold. The filtered aluminium concentrations measured at Coalburn range from 20.3 to 242 μgl^{-1} with the highest concentrations associated with storm events. The aluminium-flow relationship suggests the threshold of 50 $\mu g l^{-1}$ is exceeded when the stream flow is greater than 1 ls^{-1} and these flows occurs for more than 86 percent of the time from the flow duration curve.

The data show that for Coalburn all three standards are never met, however, the pH and aluminium thresholds are exceeded for 39 and 86 percent of the time respectively. pH and aluminium are intrinsically linked to hydrological events and when the pH threshold is exceeded it is likely that the aluminium threshold will also be exceeded too, however, the converse is not true (c.f. aluminium-flow and pH-flow relationship Figure 3.7). This implies the pH and aluminium thresholds are likely to be exceeded for at least 39% of the time.

Other characteristics such as rapidity of chemical change are important to the toxicity of an event, however, the high calcium concentrations will limit this impact, unless the changes are extremely rapid (Davies et al., 1992). Full assessment of the impact of rates of change between catchment and events is not possible due to the errors in the continuous data measurements.

The underlying Carboniferous geology and boulder clay would appear to play an important role in ameliorating the potential effects of acid episodes in Coalburn. Even during extreme events, a component of deep-water and/or sources in the peaty-gley sub-catchment must influence the stream chemistry for calcium to be present in such high concentrations. Furthermore, the acid events have been partly attributed to organic acidity from the peat in the catchment (Chapter 3) and the presence of humic material can reduce aluminium toxicity through organic complexing (Havas et al., 1984; Kullberg et al., 1993). The biological sampling supports these observations. Despite acid events at Coalburn that are apparently toxic, there is no evidence of a toxic impact on the invertebrate population (Prigg, 1994; Prigg, 1999); they are acid stressed but at sub-lethal levels.

The ameliorating factors at Coalburn appear to limit the toxic impact of acid events but this only serves to highlight the fragility of individual headwater catchment systems. Should the catchment be managed in an unfavourable manner and the ameliorating factors reduced or the same management practices were applied to a catchment without an ameliorating capacity the impacts would be deleterious.

4.3 Chemical signatures: the pH response

The duration, frequency and magnitude of acid episodes at Coalburn have been identified, this section examines the short-term dynamics observed in acid episodes and classifies the events according to their characteristics.

Flow and pH are intrinsically linked and when flow changes there is nearly always a corresponding response in pH, no matter how saturated, inundated or desiccated the catchment becomes. pH_S (pH sampled) demonstrates an exponential decay with increase in flow (Figure 3.7), although the relationship exhibits a large degree of variation of up to 2 pH units for any single flow, reflecting the complex processes governing the hydrochemical response of the catchment. The exponential decay is not merely a corollary of the logarithmic scale of pH, as the same flattening off and recovery at high flows is observed for the hydrogen ion concentration (Robson, 1993). This is consistent with the hypothesis that the catchment processes govern the pH response.

The pH_S-flow response can be divided into four distinct phases (Table 4.2), which provides a starting point for hypothesising the chemical mixing, pathways and processes occurring in the catchment. A similar classification of the Allt a'Mharciadh pH/alkalinity response was made by Jenkins et al. (1990), however, no recovery phase was observed and a three phase model was used.

The pH_C (pH continuous) times series during a storm event is surprisingly regular (Figure 4.3). There is a transient increase in pH_C (Figure 4.3) during the early phase of events with wet antecedent conditions and moderate to high flows. The initial pulse typically occurs just after the maximum rainfall intensity, and its size appears to be correlated to the maximum rainfall intensity (Mounsey & Newson, 1995). The fact the pulse occurs during the early part of an event and near the maximum rainfall intensity suggests the source is near the stream/catchment outfall or rainfall derived. Generally, the initial pulse is not observed in events that end a dry period, i.e. where base-flow produces a stream chemistry with a high pH and conductivity. This introduces seasonality into the pH_C response, with the initial pulse being more frequent during the winter months.

Table 4.2 Coalburn pH-flow separation

Phase	**Flowpaths and causal mechanisms**
1. Base-flow-Rapid decline	Under low flow conditions the stream chemistry is dominated deep-water, and while the flow may decrease there is no major change in the flowpath or the chemistry. During the early part of an event the flow increases and there is a rapid decline in pH as the deep-water is diluted by soil and peat sub-catchment water.
2. Transition.	As flows continue to increase a more complex mixing process occurs; the relative contributions from the different upper and lower soil horizons gradually change as the catchment wets up. In the transition zone demonstrates pH decreases as flow increases (but rate variable) as flowpaths switch to acidic horizons and catchment areas that make up an increasing component of the stream chemistry. The transition zone represents the most difficult catchment response to explain, with broad variation in pH for a flow reflecting: ➢ Antecedent catchment conditions. ➢ Event characteristics. ➢ Flowpath and residence time. ➢ Rising/Falling Limb Hysterisis
3. Stable low.	At high flows the catchment stabilises. As flow continues to increase the pH begins to stabilise, i.e. the catchment has established either preferred water pathways, which contribute a water of constant chemistry; or efficient mixing of the water from various sources produces a constant chemistry (Jenkins et al., 1990).
4. Recovery	During extreme hydrological events there would appear to be a recovery in the pH suggesting that rainwater (modified to some degree) may be reaching the main channel through infiltration/saturation excess (reflecting the saturated catchment conditions) or a 'washout' process is occuring.

Figure 4.3 Typical pH_c response to a hydrological event

Coalburn Event 7 21 Jan 1995

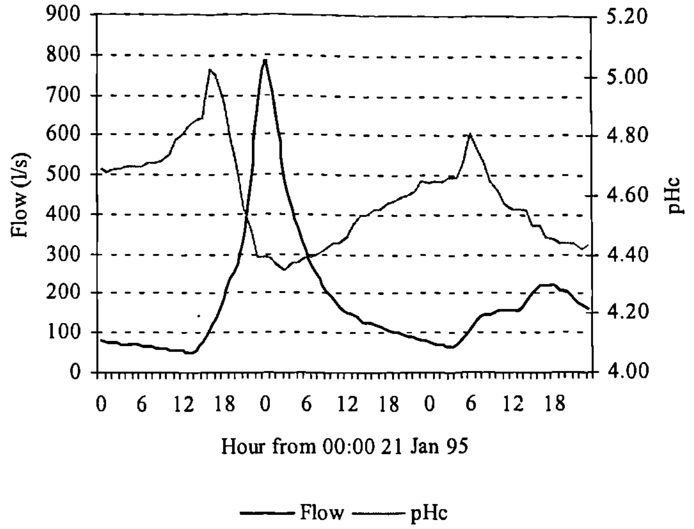
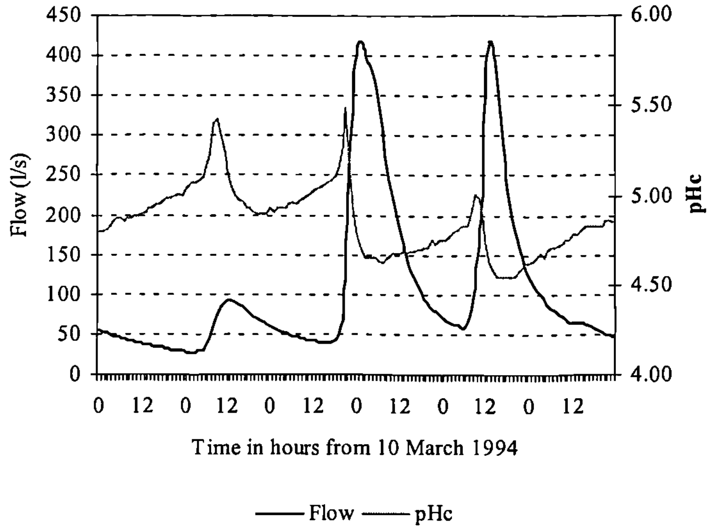


Figure 4.4 Successive decline in pH_c in a series of events

Coalburn pH_c 10 to 15 March 1994



Following the initial pulse there is a rapid fall in pH_c as the flow increases. The minimum pH_c usually lags peak flow suggesting the most acidic flowpaths do not contribute until after peak flow. This is likely to reflect the catchment shape, soil distribution; peat hydraulic conductivity; or dominance of pre-event water during an event (Soulsby, 1995a). The lag between peak flow and pH_c minimum is related to the antecedent catchment wetness and event intensity. When an extreme hydrological event occurs on a saturated catchment the pH_c

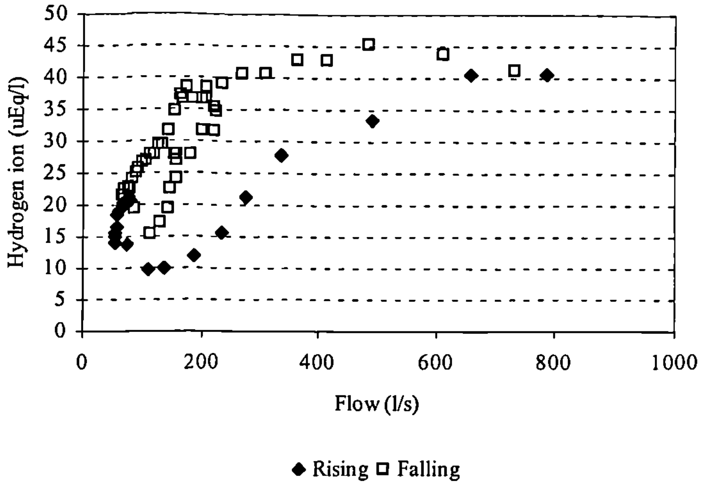
lag time is reduced and the minimum can occur before the peak flow. For example, on 31 January 1995 a large rainfall event (72 mm) occurred on a saturated catchment and the pH_c led the peak flow (Appendix I). pH_c then recovered slightly during the peak flow indicating a 'washout' process or a rainfall component reaching the stream.

At Coalburn, the pH_c exhibits a prolonged exponential recovery during recession to base-flow, despite the artificial drainage. This results from the low hydraulic conductivity of the peat soils that continue to contribute to streamflow well after an event (Robinson et al., 1998). Consequently, the longevity of acid episodes is increased at Coalburn and the recovery is often truncated by the next event, resulting in a progressive decline in catchment pH during a typical series of events (Figure 4.4). This characteristic explains the low maxima in the pH_c distribution (Figure 4.2) during winter months when the soil and peat waters dominate.

The rapid fall in pH_c during the rising limb of the hydrograph and slow recovery on the falling limb causes hysterisis in the pH_c response (i.e. during an event the pH_c for the same flows will be different depending on the phase considered- Figure 4.5). This phenomenon is a corollary of the different water sources (vertical and lateral) that contribute to the stream flow and chemistry during the different phases of an event. The distinction between the water sources and pH_c signal on the rising and recession limb may be an important signature in determining the causal mechanisms behind the events.

Figure 4.5 Hysterisis in the hydrogen ion concentration and flow relationship

(Event 7 21 January 1995)



The pH response is largely independent of the short-term variation in the rainfall quality as observed in Chapter 3. This reflects the dominance of catchment processes on the stream pH and that rapid ion exchange and solubility reactions modify the rainwater before it reaches the stream (Robson, 1993). The pH_c data would corroborate this, and even during extreme events such as 31 January 95 there was no distinct inversion of pH to suggest the rainfall was directly affecting the stream pH. Thus, as we will see below, while conductivity indicates that, on occasions, a proportion of the rainfall reaches the stream, the pH of that component is rapidly modified by catchment processes. This implies the catchment pH gradients are not over-ridden, even during extreme events with relatively short residence times, and the pH of the catchment water stores remain roughly unchanged in time and space, other than due to wetting and drying influences (Robson, 1993).

Jenkins et al. (1990), Davies et al. (1992), Robson (1993), Soulsby (1995b) and several others have observed similar pH_s-flow relationship and the characteristic pH_s/pH_c time series during storm events. However, the regular form of the pH response at Coalburn does not imply the response is consistent. This is clearly not the case with the episodic nature of the pH_c initial pulse (although it can be predicted when this will happen) and the fact that pH_c cannot be predicted from flow or vice versa. The regular pH response during an event is a corollary of the catchment structure and chemical gradients that control the source, pathway and processes. Consequently, the pH response is a good indicator of the catchment processes as observed in Chapter 3. However, the antecedent conditions and event characteristics can modify the event starting point, timing, response and impact of these so the pH_c response becomes event-specific, reflected in the variation in Phase 3 of the pH-flow response (Table 4.2; Figure 3.7).

4.4 Chemical signatures: the conductivity response

4.4.1 Definitions

Conductivity is defined as the integrated measure of the total charge in solution. The relationship between conductivity and the ionic concentration is approximated by Kohlrausch's Law (Thomas, 1986):

$$\text{Total Conductivity} = \Sigma_i \Lambda_i c_I \qquad (4.1)$$

Λ_I = Constant – the equivalent conductance of the ith ion (Scm^2Eq^{-1}).

c_I = Equivalent concentration (Eql^{-1})

The equivalent conductance for selected ions can be seen in Table 4.3, it is immediately apparent that the equivalent conductance of the hydrogen ion (350 Scm^2Eq^{-1}) is much greater than the other solutes.

Robson (1993) has previously examined the conductivity response in the Plynlimon streams and used the following approximation of total conductivity:

$$\text{Total conductivity} = 0.35\ H^+ + 0.07(\text{Cations} + \text{Anions} - H^+) \qquad (4.2)$$

where 0.35 is the equivalent conductance of hydrogen ions

0.07 is the approximate average equivalent conductance on non-hydrogen ions.

From equations 4.1 and 4.2 and the work by Thomas (1986) and Robson (1993) it is know that the important changes in conductivity, for low conductivity streams, can be linked to hydrogen ion concentrations. These occur when the pH change involves either low pH (hydrogen ions) or high pH (bicarbonate). For Coalburn, it is possible to calculate the contribution of the hydrogen and bicarbonate ions to the total conductivity from the sample data. The sample pH and conductivity are known and bicarbonate can be estimated using equation 4.3 and assuming the excess $pCO_2 = 2.5$ (Neal and Hill, 1994). The contribution of hydrogen ion and bicarbonate to conductivity can be calculated using the equivalent conductance values in Table 4.3.

Table 4.3 Equivalent conductance at 25^{oC}

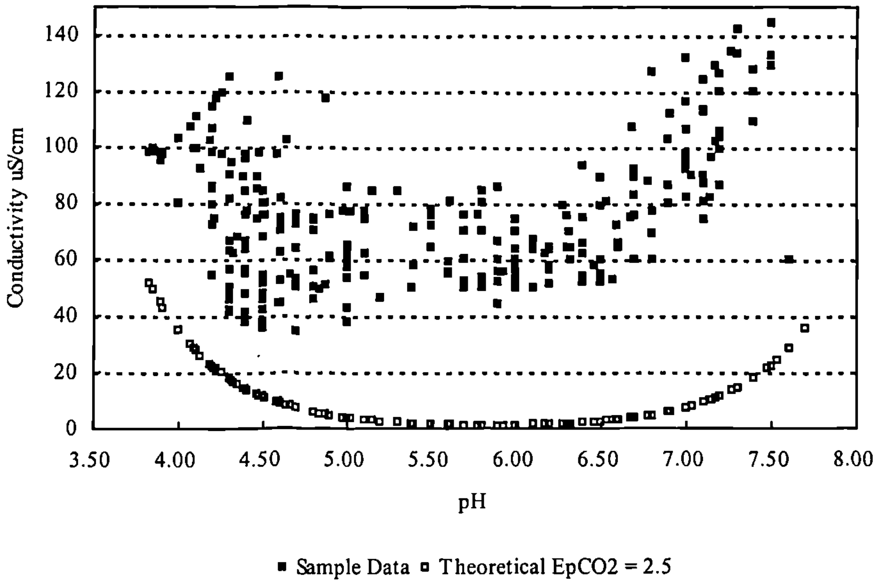
Ion	Equivalent Conductance	Ion	Equivalent Conductance
Na	50.1	NO_3	71.4
Ca	59.5	HCO_3	45.4
Mg	53.0	Al	69.0
K	73.5	Organics	40.0
Cl	76.4	H^+	349.8
SO_4	80.0		

Table from Robson (1993) Units are in Scm^2Eq^{-1}

$$HCO_3\ (\mu Eq l^{-1}) = \frac{6.25\ .\ \text{Excess}\ pCO_2}{H^+} \quad (4.3)$$

Coalburn exhibits the typical parabolic relationship between sampled pH and total conductivity (Figure 4.6), and this is clearly linked to the contributions from the hydrogen and bicarbonate components. It is apparent that while hydrogen and bicarbonate are important in driving the conductivity response, other factors such as weathering products, organics, sulphate adsorption/desorption, degassing, evaporation and dry deposition also contribute to the total conductivity (Robson, 1993). At high pH, the high total charge in solution is associated with elevated concentrations of bicarbonate, however, this does not account for all the observed conductivity and other solutes (weathering products) must contribute significantly. As pH falls the conductivity follows reaching a minima (pH 6.00 approx.), this reflects the decrease in the bicarbonate and weathering product concentrations. As pH continues to fall the conductivity increases as the hydrogen ion begins to dominate (especially where pH < 5.00), along with other ions such as aluminium and organics. This relationship between pH and conductivity is important and must be taken into account when interpreting the conductivity response and flowpaths at Coalburn.

Figure 4.6 Coalburn pH-conductivity relationship



4.4.2 Conductivity sampled

The sampled conductivity values at Coalburn have a large range (205.7 to 34.5 μScm^{-1}) and the maximum values are high in comparison with other upland streams studied in a similar manner (Robson, 1993; Neal et al., 1992). This reflects the influence of the buffering capacity of the underlying boulder clay and solid geology at Coalburn.

The overall relationship between flow and sampled conductivity demonstrates an exponential decrease as flow increases (Figure 3.7). There is a large degree of scatter in this pattern, particularly at low to medium flows, demonstrating the complex processes governing the hydrochemical response. However, this masks a complex pattern driven by the pH-conductivity relationship discussed above. At very low flows the conductivity rises to values of 150 μScm^{-1} and above, reflecting the dominance of the deep-water (and/or upwelling peat water) source. The high conductivity is due to high concentrations of base cations and bicarbonate associated with these sources. As the flow increases the deep-water sources are diluted by soil and peat sub-catchment water and conductivity exhibits a classic dilution response. However, as the flow continues to increase (or if the starting point of the event had elevated base-flow) the conductivity response is to increase as the flow increases. This response reflects the elevated hydrogen ion and aluminium concentrations that result from the increased contribution of soil and peat sub-catchment water. During extreme events, the conductivity may exhibit a dilution response due to a washout process or direct influence from the rainfall, this will be discussed in more detail during Chapter 5. The conductivity-flow response can clearly be divided into three phases as summarised in Table 4.4.

The sampled conductivity exhibits a seasonal pattern that is intrinsically linked to the dominant flowpath. During the summer months, the base-flow signature dominates the Coalburn chemistry and there is a peak in the conductivity values reflecting the dominant 'deep' flowpaths. In contrast, during the winter months the high-flow signature becomes more dominant which results in slightly lower conductivity values.

Table 4.4 Coalburn conductivity-flow separation

Phase	Flowpath/Cause Hypothesis
1. Rapid Decline.	During base-flow the conductivity increases as the deepwater (and upwelled peat water) dominates, reflecting its association with long residence times in or near to the boulder clay and elevated concentrations of weathered products. However, during an event this is rapidly diluted by soil water.
2. Increase	As flow rises an increasing component is derived from the more acidic soil waters and the hydrogen, aluminium and organic ions concentrations increase and this results in an increase in conductivity.
3.Decrease	At a threshold either a washout process occurs or the rainfall signal reaches the stream and a dilution response occurs as flow increases.

On a short-term basis, pH and conductivity are often correlated. However, while the same catchment structure and chemical gradients underlie the response, the fact that a four and three phase flow relationship is observed for pH and conductivity, respectively, implies the processes generating the response are different. Consequently, the conductivity-flow response gives another chemical signature that may provide information to unravel the causal mechanisms behind acid events. Two issues immediately arise; what causes the distinction between conductivity and pH and; what can it elucidate with respect to explaining the catchment hydrochemical response. The following section examines the continuous conductivity time series to provide more information to answer these questions.

4.4.3 Continuous conductivity

The conductivity-flow relationship (Figure 3.7) oversimplifies the Coalburn response and only when the continuous time series is examined do the short-term dynamics become apparent. The conductivity response displays two basic responses to a hydrological event, the first a dilution response and the second an elevation response (i.e. increase in conductivity) (Figure 4.7).

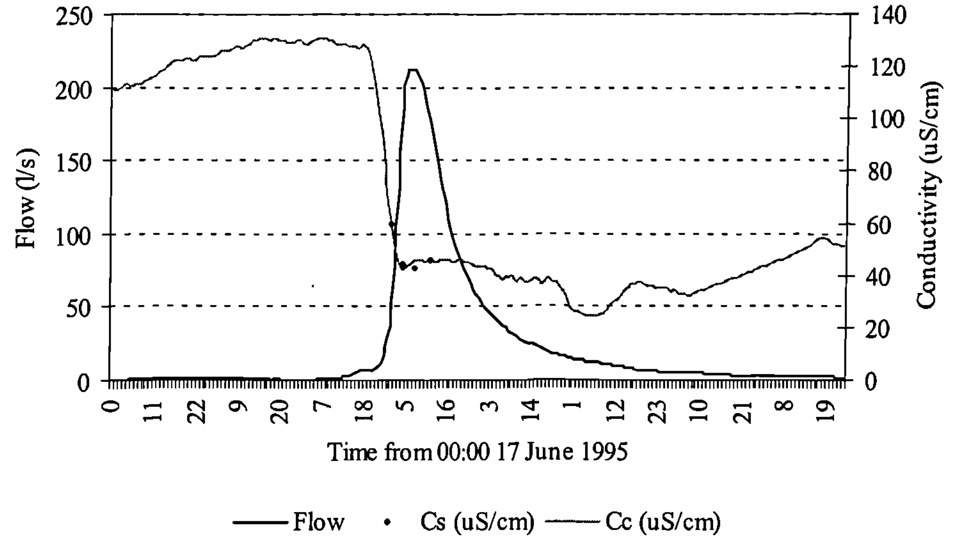
The dilution response was the expected conductivity response during an event, with the increased flow diluting the solutes as per the conductivity flow relationship (Figure 4.7). The response is consistent with the catchment gradients, with the high conductivity deep-water being diluted by the lower conductivity soil water. The typical response shows no initial pulse, a rapid decline in conductivity on the rising limb and a minimum at approximately peak flow (i.e. the time of maximum dilution). The conductivity then recovers slowly, reflecting the hydrological conditions and, as with pH_c, this can be truncated by the subsequent event. Similarly, the conductivity response shows hysterisis between the rising and falling limb, implying that different water sources or mixes of water sources are contributing during each phase of the hydrograph.

The dilution response generally occurs when a small to medium sized hydrological event occurs following a prolonged dry period. As a result, the dilution response is observed more in the summer months, introducing seasonality to the short-term dynamics.

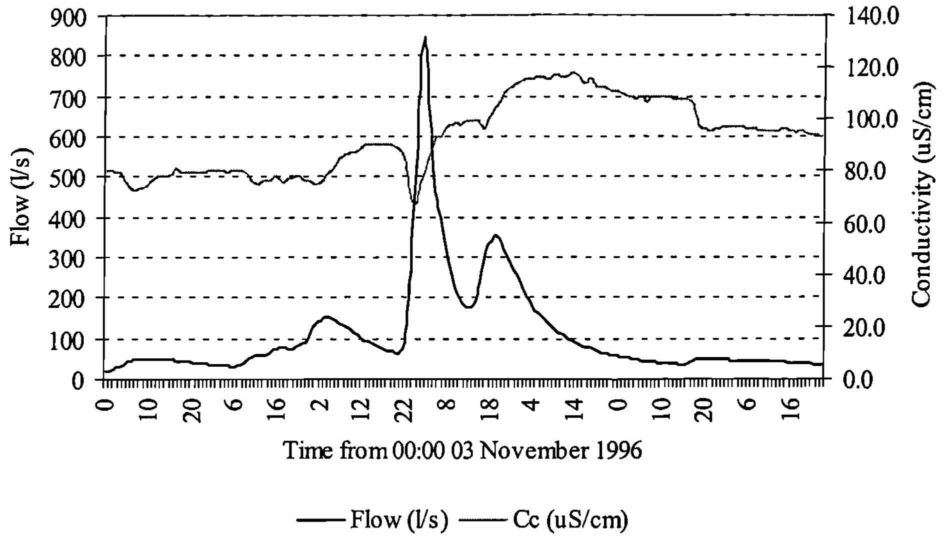
The mechanisms that cause such a response are discussed fully in subsequent chapters; however, the response is partly linked to the pH-conductivity relationship (Figure 4.6). Under base-flow conditions, the stream has a high conductivity reflecting the elevated base cation and bicarbonate concentrations in the deep-water. During the event the increasing soil water contribution dilutes the base cation and bicarbonate concentrations and, while the pH decreases it is rare that a small/medium event will depress the pH below 5.00. Consequently, the conductivity response is restricted to the Phase 1 ‘dilution’ phase of the pH-conductivity curve (Figure 3.7; Table 4.4) and conductivity falls as flow increases. Where a larger event ends a dry period then a dilution response may be observed initially, however, if the pH goes below 5.00 then conductivity may begin to rise (Mounsey & Newson, 1995).

Figure 4.7 Coalburn conductivity responses

Conductivity dilution response



Conductivity elevation response



The dilution response is not a function of the pool effect discussed in Chapter 2, as this indicated conductivity in the pool was less than the stream sample. Hence, if the pool effect were operating the conductivity would be expected increase initially. However, the pool effect exacerbates the diurnal variations in the pH and conductivity during base-flow periods that result from heating of the weir pool.

The second conductivity signal, the elevation response, exhibits an initial transient fall in conductivity during the early part of an event that coincides with the initial pH_c signal peak. As the flow increases, the conductivity rises, generally reaching a maximum following peak flow, which coincides with the minimum pH_c (Figure 4.7). As an event recedes the conductivity slowly decreases and returns to the pre-event level, reflecting the continued dominance of peat sub-catchment and soil water (i.e. the low hydraulic conductivity of the peat continues to contribute well after the event). As the flow subsides, the conductivity may then increase if the deep-water begins to dominate; alternatively, the 'recovery' may be truncated by the next event.

The conductivity elevation response generally occurs following wet antecedent conditions, i.e. the catchment is saturated. Under these circumstances, an elevation response has always been observed although the exact nature of the response may be modified by the event intensity (see Event 9 Chapter 5). The mechanisms causing the conductivity elevation response will be discussed in subsequent chapters, however, it is linked to the pH-conductivity relationship (Figure 4.6). During wet periods, the 'base-flow' is elevated due to the increased contribution for the soil and peat sub-catchment waters, resulting in the Coalburn pH and conductivity being low at the onset of an event. Even a relatively modest runoff event can depress the pH well below 5.00 and as observed from Figure 4.6 the increase in the hydrogen ion concentration (and other ions) will result in a concomitant increase in conductivity. The conductivity response is modified during extreme events when a direct rainfall or washout process influences the conductivity and a dilution response can then becomes evident during these circumstances.

A link was established between the input and stream chemistry in this, and others, study for the chloride and conductivity signature (Chapter3; Robson, 1993). In essence, this served to highlight that a rainfall event or pollution climatology could impart a conductivity and chloride signature on the water stores within the catchment. After the event ceases the catchment water reservoirs retain the conductivity/chloride signature of the preceding storm. Subsequently the stream and event chemistry are influenced by this signature; however, as time progress the signature becomes diluted by other events and modified by catchment processes. The other solutes exhibited no significant relationship between the rainfall and stream chemistry due to modification by catchment process (Chapter 3). However, because conductivity is a measure of the total ionic strength it implies this process may have some influence on the other solutes, and the lag factor needs to be taken into account when considering the relationships. By taking into account the lag factors, one is essentially calculating the residence time within the catchment stores: useful information when considering the flowpaths in the catchment.

The effects of conductivity conditioning across the catchment gradients and water sources are likely to be different. For the deep-water component percolation of the wet, occult and dry deposition signal through the soil profile is likely to buffer any major changes in the deep-water chemistry though conditioning. In contrast, the shallower soil-waters will be more susceptible to conditioning as there is less residence and buffering time, and they are therefore likely to be modified to a greater extent by the rainfall chemistry. Thus, the conditioning of conductivity and chloride may be seasonal, with this mechanism being more important during the winter months when the soil-water is dominant. When an extreme event occurs on a saturated catchment (i.e. catchment storage is at capacity) an element of the rainfall conductivity signal may be observed in the stream and the catchment conductivity gradients breakdown. However, no similar observations were made for pH due to rapid modification by catchment process. This implies that while, under such conditions, the rainfall signal may reach the stream, the pH signal will be modified and the conductivity will retain an element of the rainfall signal.

At Coalburn, the linkage between rainfall and stream chemistry has only been observed during a few extreme events with distinct chemical signatures (i.e. high conductivity values in inputs (Chapter 3; Figure 3.8)). For 'regular' events the linkage has not been observed, which suggests the catchment has a large storage capacity that damps the signal. The rainfall conductivity signal will also be smoothed by the rainfall sampling frequency and the small differences that would be indicative of such an effect are of a similar order to the error band-width of the continuous conductivity measurements. Therefore, it would be difficult to attribute a trend to pollution climatology and catchment conditioning alone.

The hypothesis that the catchment has relatively large storage capacities and long lag times for certain flow components is supported by the fact the process of conductivity conditioning of the water stores does not appear to over-ride the catchment chemical gradients that underlie the conductivity response. If the rainfall chemistry were driving the catchment conductivity response, more variation would be expected, as would stronger relationships between rainfall and stream-flow solute concentrations.

At Coalburn the regular conductivity response(s) during an event are a corollary of the catchment structure and the processes that operate during an event setting up the basic chemical gradients in the catchment. However, the antecedent conditions, event characteristics and to some extent the pollution climatology modify the conductivity of a catchment store and its residence time, that then influence the conductivity response. Neil (1992) and Robson (1993) have observed similar conductivity responses. Robson (1993) has observed a transient fall in conductivity at the onset of an event for the Afon Hore; however, after extensive rainfall the initial fall was not observed, implying it was more common in summer. This contrasts with Coalburn, where an initial fall is observed during events with wet antecedent conditions and this coincident with a pH increase (not seen on Afon Hore) suggesting a different process may be operating.

4.5 Summary

The continuous pH and conductivity data provide a clearer picture of the acid episodes and allow a more detailed analysis of the short-term catchment scale dynamics, which lie behind the duration, frequency, and magnitude of the events. In terms of the analysis, it has elucidated the following aspects:

Assess the episodic acidification status of the Coalburn catchment and determine the magnitude, duration and frequency of the acid events.

The continuous pH (pH_c) time series clearly displays acid episodes associated with most hydrological events, and these have been observed to reach a minimum of pH 3.3 (sampled data) that would suggest the events are thoroughly toxic. In summary:

- The pH_c **duration** indicates that Coalburn is acidic (i.e. $pH < 5.5$) for 39% of the time and is very acidic ($pH < 4.5$) for 8.5% of the time. The duration histogram (Figure 4.2) exhibits a double maximum reflecting the catchment structure and seasonal variation in the water tables. During winter the acidic shallow flowpaths dominate producing the lower maxima, while during summer the deeper well-buffered flowpaths dominate producing the higher maxima.

- Analysis of the **frequency** of acid episodes at Coalburn revealed that there were 95 events between 1994 and 1997 where the pH was less than 5.5. This frequency initially appears low, however, this is explained by the long duration of the events. If the threshold for pH is decreased to 5.0 and 4.5 the frequency of events during 1994 to 1997 was 120 and 119 respectively, and while the events are more frequent their duration was shorter.

- The **magnitude** of acidification was considered against the Freshwater Fish Directive (78/659/EEC) and Surface Water Abstraction Directive (75/440/EEC) standards; Coalburn would generally not comply with the environment quality standards set in either. To assess the biological importance of acid episodes the chemistry was compared to critical pH, calcium and ionic aluminium concentrations. At the catchment outfall Coalburn exceeded the pH and aluminium thresholds for 39 and 86 percent of the time respectively. However, all three thresholds were never exceeded, due to the high calcium concentrations derived from the underlying geology. The high calcium concentrations and the organic content of the Coalburn waters play an important role in ameliorating the biological impact of the acidity at Coalburn.

The duration-frequency-magnitude analysis applied to the Coalburn pH data has revealed that Coalburn clearly exhibits acid episodes that while being less frequent than expected had a longer duration due to the influence of the peat soil. The acid events lead to failures of environment quality standards and the pH and aluminium concentrations would suggest the acid events should be toxic, however, the elevated calcium concentrations and organics reduce the biological impact. The analysis has highlighted the duration-frequency-magnitude are intrinsically linked and to assess the impact on the stream they all need to be considered in terms of several solutes including pH, aluminium and calcium. Simply considering one component may lead to an incorrect conclusions and management decisions.

The benefit of collecting continuous pH_c (and conductivity) data is clearly apparent. The data provides extensive information on the duration, frequency and magnitude of the acid episodes. Given the data are of reasonable accuracy, it is an improvement on deriving extreme values from applying an appropriate statistical technique to a limited number of spot samples; it effectively removes the dilemma of what is an appropriate technique. Furthermore, the continuous data captures short-term dynamics such as the initial pulse that would be difficult, or impossible, to capture even with the most intense sampling regime. The down side to the collection of continuous pH_c and conductivity data is the infrastructure, maintenance and analysis time required (all of which have a cost) to ensure the data is of reasonable accuracy.

Identify the important short-term chemical signatures and variations in the Coalburn catchment and determine their value in conceptualising the processes underlying the acid episodes.

At Coalburn, a regular response was observed for the pH and conductivity during hydrological events and this has been intrinsically linked to the catchment structure, flowpaths and chemical gradients. During each phase of a storm event, the pH and conductivity response are generally conceptualised as a product of varying proportions of the chemically different soil, deep, peat and peat-gley water (and the gradient across these). While the same hydrological mechanisms underlie both the pH and conductivity responses, there are fundamental differences in their chemical response, which affects how the signatures can be interpreted. The fact they are different is advantageous as each signature can be used as an additional source of information to elucidate on the causal mechanism of an event.

Flow, pH and conductivity are intrinsically linked and when flow changes there is nearly always a corresponding response in pH and conductivity. The pH_s-flow response can be divided into four distinct phases, while the flow-conductivity response can be divided into three phases. Both can be explained by varying mixes of the catchment water sources (Tables 4.2 and 4.4)

The pH_c (pH continuous) times series during a storm event is regular, however, this should not be assumed to imply the response is consistent. This is demonstrated by the episodic nature of the pH_c initial pulse and the fact that pH_c cannot be predicted from flow or vice versa. The regular pH response is a corollary of the catchment structure that controls the source, pathway and processes that operate during any phase of an event. However, the antecedent wetness and event characteristics can modify the event starting point, timing, response and impact of these so the exact pH_c response becomes event specific (Table 4.5).

In contrast, conductivity displays two basic responses to a runoff event, the first; a dilution response that follows dry antecedent conditions and is more frequent in summer. The second is an elevation response that has a transient initial fall; it occurs with wet antecedent conditions, and is more frequent during the winter months. The conductivity response is controlled by the catchment structure but the exact response can be modified by the antecedent wetness, pollution climatology and event characteristics (Table 4.5). Another important factor controlling the nature of the conductivity response is its relationship with the bicarbonate and hydrogen ions. While conductivity data provide valuable information for this study, there is evidence that they could be utilised further, particularly in estimating effects of pollution climatology and residence time. To fully utilise the conductivity for this improved field equipment would be required so that accurate continuous conductivity monitoring of both the rainfall and catchment outfall could be carried out.

Table 4.5 Modification of the Coalburn pH and conductivity response

	Antecedent Wetness	**Pollution Climatology**	**Event Conditions**
pH Response	Wet antecedent conditions are signified by an initial pulse. The same pulse is not evident with dry antecedent conditions.	Catchment processes dominate the pH response. There was no evidence of linkage between rainfall and stream pH. Even during extreme rainfall events rapid modification of rainfall pH occurs.	Catchment gradients and processes dominate. Even during extreme events, there is only a slight recovery. The intensity and magnitude of an event is positively correlated with the rates of change and severity of the acid episode.
Conductivity Response	Wet antecedent conditions are signified by an initial conductivity fall, which is not evident with dry antecedent conditions.	There is evidence that when high values of rainfall conductivity impact on the catchment they can be observed in stream chemistry. This implies the pollution climatology can affect conductivity during and following an event. However, this does not over-ride the catchment gradients or occur for less extreme events.	Catchment gradients and processes dominate. However, during extreme events the rainfall signal may reach the stream and result in a recovery. The intensity and magnitude of an event is positively correlated with the rates of change and severity of the conductivity response.

The patterns observed in the linkage between the rainfall and stream conductivity reveal/infer some important characteristics of the processes operating in the Coalburn catchment. For small/medium rainfall events, the rainfall signal did not appear to reach the stream. This implies much of the water entering the catchment remains in the catchment stores and influences the subsequent events, which suggests that events are dominated by pre-event water. However, when the catchment is saturated and the water stores are at capacity the rainfall signal may reach the stream and an element of event water contributes to the hydrochemical signal. This is consistent with the observations of Robson (1993) in that the stream hydrochemical response to rainfall is better viewed as a function of the mix between the various stores of water in the catchment and in terms of residence times.

5 Coalburn: The catchment hydrochemical response.

Overview

The hydro-chemical patterns observed in the Coalburn catchment have been discussed in terms of what they elucidate with respect to the chemical signatures, flowpaths and the processes which generate the catchment scale response, albeit at the 'black box' level of rainfall/cloud mist inputs and streamflow outputs. The examination of Coalburn hydrochemistry data during events has been limited to a generic examination of the pH and conductivity response. This chapter utilises the information gathered in this and previous Coalburn studies to explore the following topics:

- *To classify Coalburn hydrochemical events according to their catchment scale response, characteristics and signatures.*
- *Application of hydrological principles and chemical signatures to conceptualise the likely causal mechanisms underlying the acid events at Coalburn (considering the pollution climatology, flowpaths, residence times, antecedent conditions and the role of event and pre-vent water).*
- *To produce a conceptual runoff model for the Coalburn hydrochemical response.*

Exploring these topics will move our understanding of the mechanisms generating the hydrochemical response in the Coalburn catchment to the 'grey box' level; these hypotheses will then be tested further in Chapter 6.

5.1 Processes generating the hydrochemical response in the Coalburn catchment

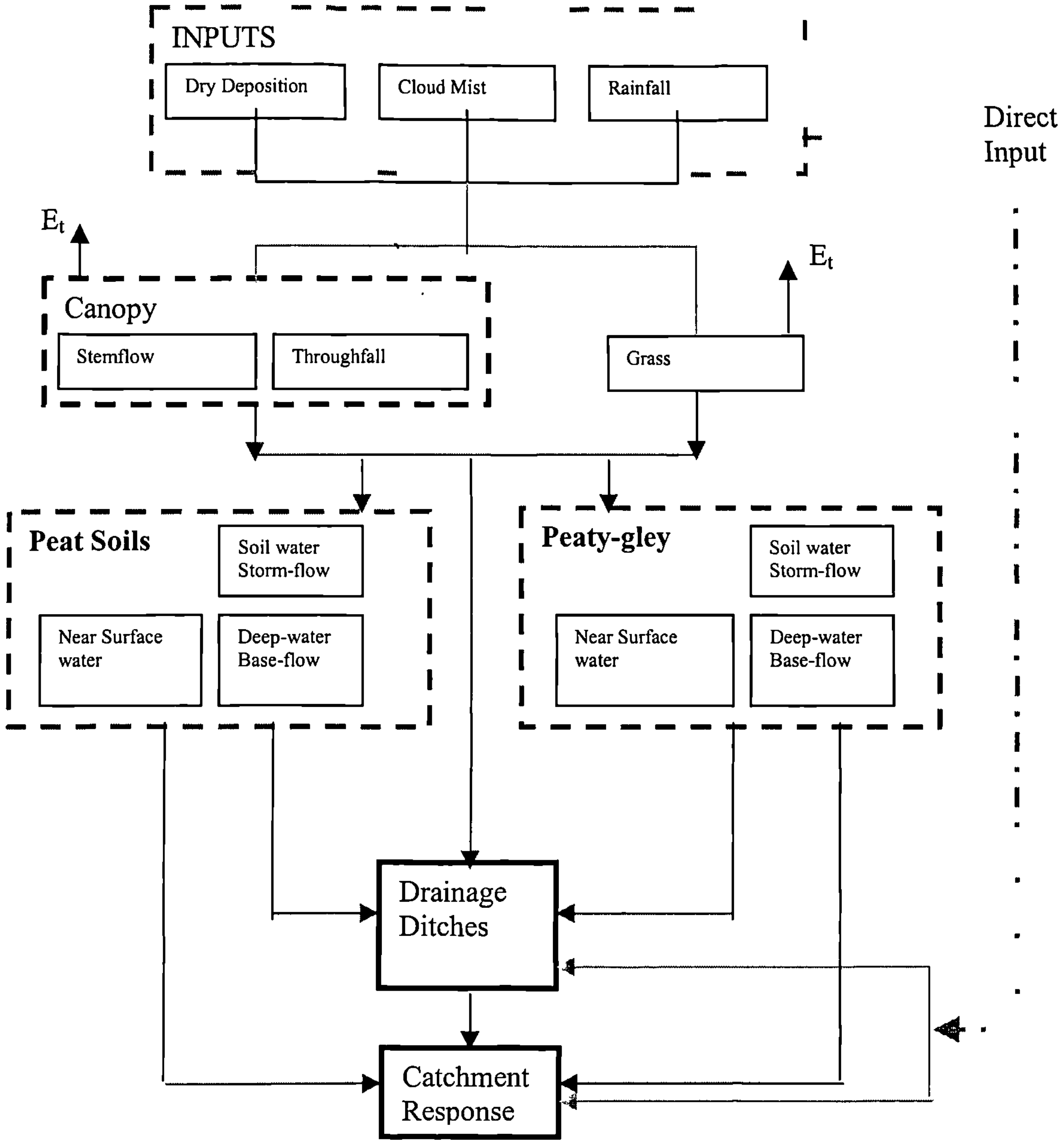
The basic water quality characteristics at Coalburn depend upon the input quality which is then modified by the canopy, soil and underlying geology (Jenkins et al., 1990). Superimposed on to this, variations in the basic stream chemistry are accounted for by the hydrological pathways, residence times and mixing of water from different sources under a variety of flow conditions.

The processes responsible for the flowpath, residence times and mixing of water are dynamic, being subject to changes on varying timescales from seasonal to event based, which implies the hydrochemical response at Coalburn could be infinite. Nevertheless, regular patterns have been observed in the Coalburn hydrochemical response; consequently, it should be possible to classify the events according to these patterns. However, before this analysis can be carried out it is necessary to have an understanding of the processes that influence the hydrochemistry during an event.

The hydrochemical response at Coalburn, and similar catchments, is controlled by four fundamental parameters: antecedent conditions (moisture and pollution climatology); event precipitation characteristics and storm hydrograph; flowpaths; and residence times. These are briefly examined in general and in terms of the information presented so far in this thesis.

To facilitate the understanding of the causal mechanisms driving the Coalburn catchment hydrological and hydrochemical response an elementary hydrological runoff model, similar to the Birkenes Model (Christophersen et al. 1990), has been employed as the first step to moving towards a much fuller conceptual model for Coalburn (Figure 5.1). The model was derived from fundamental hydrological processes observed in forested catchments. The model was then tailored to the Coalburn catchment using the hydrochemical patterns observed in the previous chapters (e.g. the direct influence of rainfall as observed by the relations between chloride in the rainfall and stream).

Figure 5.1 Coalburn runoff model



Key

E_t = Evapotranspiration

5.1.1 Antecedent weather and catchment conditioning

The catchment hydrological/hydrochemical response to an event is partly a function of the antecedent catchment wetness. In terms of the hydrological model (Figure 5.1), this controls the event storage dynamic and the starting point of the subsequent processes that operate during the event. For example, the catchment response to an event falling on a saturated catchment is very different from one on a dry catchment. At Coalburn this is demonstrated by the relationship between solute concentrations and flow. At high-flow the concentrations are very different from those at base-flow, reflecting the different processes operating at the two extremes, while intermediate events represent a mix of the two.

The wind direction and proportion of the time from that direction was shown to have a significant bearing upon the antecedent conditioning of the Coalburn catchment in terms of the wet and occult deposition (and inferred dry deposition). Two chemical signatures were identified from the precipitation and cloud mist. The first, was the terrestrial source signature from the easterly sectors that yielded precipitation / cloud mist that was more acidic in terms of pH (precipitation 4.81; cloud mist 3.77) and acid anions. The second, marine signature was characterised by high pH and elevated concentration of marine ions.

A linkage between conductivity (and chloride) in rainfall and stream water chemistry has been observed at Coalburn. This implies the pollution climatology/catchment conditioning may effect the character of the subsequent event, and during extreme events it may impact directly on stream chemistry (the direct input in Figure 5.1).

5.1.2 Event precipitation characteristics and the storm hydrograph

The antecedent conditions control the hydrological/hydrochemical starting point of the event. However, it is the event characteristics in terms of precipitation type, quantity and intensity that drives the catchment response (i.e. this controls the flowpaths and residence times).

Valuable information can be obtained from some elementary hydrological analysis. Calculating the precipitation inputs and catchment yields will allow an assessment of how much of the incident precipitation contributes to the event or to the catchment deficit, giving an indication of the residence time. If hydrograph separation is carried out this will enable the flow to be separated into base-flow (Q_b) or storm flow (Q_s) components and this will gives an indication of the flowpaths operating.

5.1.3 Flowpaths

The volumes and flowpaths (throughfall, stemflow, deep-water, soil-water etc.) have been highlighted as a principal control of surface water chemistry (Davies et al., 1992; Langan, 1989). Solute pathways are inferred from both the hydrological pathways and by direct comparisons between percolate and streamflow chemistries (Chappell et al., 1990; Waterfall, 1994). The varying contributions and timings of water from similar/differing source areas are critical to the chemical composition of the stream water (Davies et al., 1992; Soulsby, 1993; Soulsby 1995b).

The Coalburn model (Figure 5.1) highlights the complexity of identifying the flowpath taken by the precipitation after it enters the catchment. The previous chapters have attributed chemical signatures to the key flowpath components in the model (Table 5.1). However, the catchment response integrates these signatures and it is difficult to then unravel the exact flowpaths and sources operating when 'back casting' from the stream chemistry alone. This process is further frustrated by the fact the flowpaths and a components chemical signature may not be constant; varying in time and space.

Coalburn chemistry is broadly consistent with the two-component mixing regime typical of catchments with a substrate of high buffering capacity and organic rich peat surface horizons. Accordingly, Coalburn stream has distinct chemical signatures under base-flow and storm flow conditions. From these signatures and soil profiles (Hind, 1992; Waterfall, 1994; Baglee, 1994) it can be inferred that the base-flow component is derived from deep-water, while the storm-water chemistry is a mixture of deep-water and soil water. The base and storm flow chemical signatures are summarised in Table 5.1.

In addition to the vertical gradients in flowpath chemistry, the Coalburn catchment exhibits distinct spatial patterns in water chemistry according to the catchment soil patterns. Consequently, the lateral flowpaths/source area must be considered when hypothesising the casual mechanisms of the hydrochemical response. The lateral flowpath can be classified according to the chemical signatures from the two main soil types in the catchment, i.e. peat, peaty-gley or a mixture of the two, the signatures of which are summarised in Table 5.1.

Table 5.1 Chemical signatures of hydrological component and flowpaths

Signature	Characteristic
Throughfall (Hind, 1992; Wake, 1994)	Compared to incident rainfall the throughfall generally has lower pH, higher conductivity and concentrations of Ca, Mg, Na and K.
Stemflow (Hind, 1992; Wake, 1994)	Compared to incident rainfall and throughfall generally has lower pH, higher conductivity and concentrations of Ca, Mg, Na and K. The stemflow chemistry is different for trees growing on the different soils: Mn and K concentrations are believed to be greater on the peaty-gley soils, while the stemflow is more acidic on the peat soils.
Base-flow	High pH; high conductivity; base cations rich and positive alkalinity
High-flow	Low pH; lower conductivity; base cation depleted and decreases colour; increased aluminium and negative alkalinity
Peat-soil	Low pH; low conductivity; base cations depleted; elevated aluminium; elevated TOC/DOC; coloration and negative alkalinity
Peaty-gley	High pH; high conductivity; elevated base cations; little coloration and positive alkalinity.

Volumetric hydrograph separation, in terms of flow, has been considered above as an indicator of flowpaths. Neal et al. (1992) and Robson (1993) have successfully applied a two-component mixing model of base-flow and storm flow chemistry to explain the Plynlimon response. Jenkins et al. (1990) adopted a three component separation for Allt a'Mharcaidh, classifying the response into the base-flow, whaleback and quick-flow components. Conceptually the three-component system implies the underlying base-flow is fed from the relatively constant base-flow, whereas the whaleback component of the response represents the slow wetting of the soils in response to rainfall and slower draining of soils during wet periods. The quick flow represents the sharp hydrograph peaks that are a result of preferential pathways operating during storm events. (The relative magnitude of the peak depends on the timing in relation to the position on the whaleback).

The separation of the Coalburn hydrochemical response for pH_s-flow response produced four distinct phases (Table 4.2), while the conductivity-flow response can be divided into three fundamental phases (Table 4.4). These differences reflect the mechanism/processes generating the pH and conductivity response (cf. Chapter 4). When analysing the events the hydrograph separation and runoff model should be utilised to ascertain the likely source of water in terms of depth and location in the catchment. The physical source of the water can then be cross-referenced with the chemical response (and hydrochemical separation) to verify the water source and pathway. This process is difficult for the third (pH) and second (conductivity) phases of the catchment response where variability in the water quality for a given flow depends on the mixture of sources and flowpaths observed. Furthermore, the chemistry of the stores is not constant over time and varies according to antecedent and event conditions.

5.1.4 Residence time

In addition to the volumes and flowpaths, the residence time of water within each contact zone and flowpath controls the resultant surface water chemistry (Davies et al., 1992; Langan, 1989). Each flowpath component has a chemical signature and an input to that component is likely to be modified (i.e. pick up that stores chemical fingerprint) to varying degrees proportional to its residence time. The effect of residence time has been demonstrated in the link between the rainfall and stream water chemistry; long residence times may imply the rainfall has little effect on the stream chemistry as the catchment almost completely modifies the inputs. For moderate residence time the effect may be seen in the subsequent event, while during extreme events (i.e. short residence times) the effect may be observed during the event.

The residence time of water within the catchment can be thought of in terms of varying contributions from event water, generally derived from the rainfall, soils and upper horizons, and pre-event water derived from the deeper and riparian zones (Chappell et al., 1990). The proportions of event and pre-event water vary with antecedent conditions, the catchment soil moisture regime and catchment conditioning (Davies et al., 1992).

There is some debate over whether event hydrochemistry is dominated by event or pre-event water. The discussions in Chapter 3 and 4 would suggest that at Coalburn there is a predominance of pre-event water during small/medium events, however, during extreme storms event water may reach the stream (Soulsby, 1995b). Robson (1993) and Neal & Rosier (1990) have shown that the proportion of rainfall passing directly through the

Plynlimon catchments at the event scale is relatively small; a hydrological event promotes rapid displacement of pre-event water from within the catchment.

5.2 Classification of acid episodes at Coalburn

The sampled and continuous pH and conductivity response at Coalburn have been described as being regular but not consistent, with the following characteristics being variable:

1. The presence of an initial pH and conductivity pulse.
2. The conductivity dilution or elevation response.

Other characteristics may vary between events, for example the rates of change; however, as previous discussions have emphasised, the current instrumentation cannot provide data of sufficient accuracy to be able to determine such trends. This frustrates what may have been a fruitful aspect of research until the instrumentation is improved.

The Coalburn pH response reflects the basic structure of the catchment and processes occurring within the catchment, while the conductivity response is affected by the catchment structure/processes as well as antecedent conditions. The catchment physical structure is fixed (for these timescales) which implies variations in the catchment response must reflect more transient factors including the flowpaths, antecedent conditions, residence times and event characteristics. The flowpaths are in essence fixed by the catchment structure but the dominant flowpath depends on the antecedent moisture conditions, residence times and event characteristics which are variable. Consequently, it should be possible to classify hydrochemical events according to these variable factors, enabling analysis of a generic classification of events, rather than having to examine events on an individual basis.

Mounsey & Newson (1995) carried out a preliminary classification of Coalburn acid episodes using the antecedent wetness and precipitation intensity. Whilst this classification is adequate the categories should be broadened to antecedent conditions and event conditions, consequently the hydrochemical response can be classified according to the matrix in Table 5.2.

Table 5.2 Coalburn acid event classification system

	Event Conditions			
Antecedent Conditions	Normal Rainfall	Intense Rainfall	Snow or Snow Melt	**Antecedent Conditions**
Wet				Terrestrial
Dry				
Wet				Marine
Dry				

Antecedent conditions were subdivided, firstly, according to catchment wetness (wet/dry) which affects the storage dynamic and hydrological conditioning of the catchment, and, secondly, according to the antecedent wind direction (terrestrial/marine) that affects the chemical conditioning of the catchment. This represents the starting point of an event.

The event conditions were subdivided according to the precipitation intensity (normal, intense and snow) which is an important factor in controlling the hydrological response of the catchment and the dominant flowpaths during the event.

This results in twelve generic event categories for classifying Coalburn events; however, the 'snow' category does not occur frequently at Coalburn. The following sections examines the characteristics of hydrochemical events at Coalburn, discusses the causal mechanisms behind those events and examines whether classification according to the above criteria (Table 5.2) is possible through observable differences between the events.

5.3 Dry Antecedent Conditions (DAC)

During dry periods the continuous conductivity and pH rise and the subsequent event typically exhibits a pH decrease and a dilution response in the conductivity. Examples of events with dry antecedent conditions (DAC) and a dilution response were chosen where both sampled and continuous data are available. Given the dry antecedent conditions the events can then be sub-classified according to the other criteria in Table 5.2, namely pollution climatology and the event characteristics (i.e. rainfall intensity).

5.3.1 Event 1 19 June 1995 DAC / marine / low intensity

The antecedent weather was dry and this was reflected in the antecedent wetness indicators with an API of 23.1 mm and pre-event flow of 0.61 ls^{-1} (Table 5.3).

The pollution climatology was mixed prior to the event, with marine winds dominating the previous six days, and the rainfall chemistry for the period 16 June – 21 June exhibited a marine signature with high pH and sea salt concentrations. Prior to the event, the stream chemistry showed the typical base-flow signature with high conductivity, pH and base cation concentrations.

The rainfall event resulted from the passage of a frontal system. The total rainfall entering the catchment was of relatively low 25.8mm (38.7 Ml). With the onset of rainfall, the catchment did not immediately respond, it was approximately an hour before the flow increased, to be expected given the canopy and soils were dry and a proportion of the rainfall had to make up these deficits prior to contributing to streamflow.

The catchment response can be seen in Table 5.3, Figure 5.2 and Appendix A. There was a slow increase in flow during the first rainfall, with the flow remaining constant for three hours. With the onset of the second rainfall, the flow rapidly increased to a maximum of 212 ls^{-1}, lagging the maximum rainfall intensity by three hours. The rainfall then began to abate and flow receded.

Hydrograph separation (Table 5.3) indicates that 27% of the incident rainfall made up the storm flow component and during the event a total of 34% of the incident rainfall was discharged at the catchment outfall. Consequently, most of the water entering the catchment was retained/utilised in making up the catchment deficits. This implies pre-event water dominated with the dry catchment promoting the retention and vertical movement of water.

The event conditions gradually wetted a dry catchment, and the hydrochemical response was a dilution response in the conductivity and an acid episode in the pH reflecting the dilution of the base-flow component by the soil water (Appendix A).

It was several hours after onset of rainfall before a hydrochemical response was observed; reflecting the hydrological conditions. There was no initial pulse in either the pH_c or conductivity, which has been observed in other events. The initial pulse will be discussed in more detail later, however, the fact it is not observed under these conditions may provide valuable information in interpreting the mechanisms causing it.

Table 5.3 Event 1 19 June 1995

Hydrological Response	**Event 1** **19 June 1995**
Antecedent Conditions	
API (mm)	23.1
Pre Event Flow (ls^{-1})	0.61(19/06 at 0400)
Pre Event pH	7.67
Pre Event Conductivity	130
Prior wind direction	Mainly Marine
Event Conditions	
Rainfall Total (mm)	25.8mm Two burst of 14.2 and 16.6mm
Maximum intensity (mm hr^{-1})	2.4 (20/06 at 0000)
Total Volume Input (Ml)	38.7
Maximum Flow (ls^{-1})	212 (20/06 at 0700)
Number of peaks	1
Total Flow Output (Ml)	13.12
Runoff ratio (%)	34.0
Storm flow (%)	7.1
Base-flow (%)	26.9
Event wind direction	Mixed
Continuous Hydrochemical Response	
pH_c pulse	No
pH_c Max/Min	7.67/5.02
pH_c fall during event	2.65
Does pH_c lag/coincide/lead	Lag (6 hours)
Conductivity Fall Pulse	No
Conductivity Max/Min	130/42
C_c rise/fall during event	88 (Fall)
Does C_c lag/coincide/lead	3 (Lead)

Solutes			
Calcium (μEql^{-1})	↓	↓	↓
Magnesium (μEql^{-1})	↓	↓	↓
Potassium (μEql^{-1})	■	↑	↓
Sodium (μEql^{-1})	■	↑	↓
Chloride (μEql^{-1})	ND	ND	ND
Sulphate (μEql^{-1})	ND	ND	ND
Aluminium ($\mu Moll^{-1}$)	↑	↓	↓
Iron ($\mu Moll^{-1}$)	↑	↑	↓
DOC (mgl^{-1})	↑	↑	↑
Colour (mgl^{-1})	■	↓	↑

Key to solutes

Concentration on rising limb	Concentration at peak flow	Concentration on falling limb

↑ Concentrations increasing.
↓ Concentrations decreasing.
■ No pattern. ND No data.

The initial pH_c was relatively high (7.67) and with the onset of rainfall it fell slowly during the first rainfall (Figure 5.2). As the flow began to increase rapidly the pH_c fell to a minimum of 5.02 ($pH_s = 4.80$) lagging peak flow by six hours. The relationship between the rate of change of flow and pH_c was expected. On the rising limb the increase in flow is in response to greater volumes of water derived from the acidic soil water horizons and peat sub-catchment, diluting the deep-water. Consequently, the faster the rise in flow the more rapid the decline in pH_c.

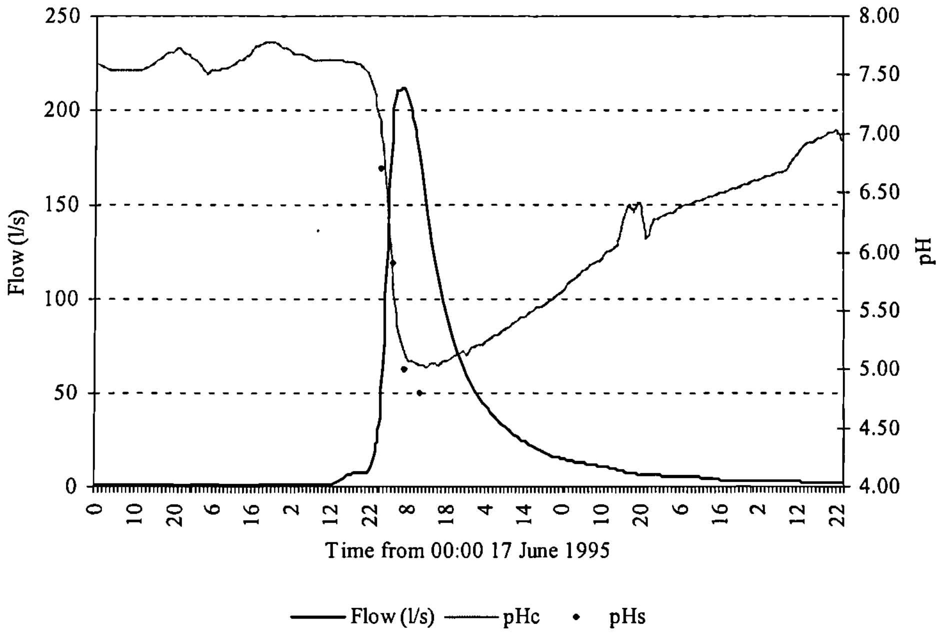
Interestingly, the dilution of the deep-water component by acidic sources continued until well after peak flow. This indicates the maximum input from the soil water component and/or the contribution from the more acidic peat sub-catchment (located further away from the sampling site) do not occur until later. This response suggests that during much of the event the pH_c response was dominated by pre-event water and it is not until the later stages that event water contributes, if at all.

On the recession limb, pH_c recovers slowly, reflecting the hydraulic properties of peat in the Coalburn catchment that continues to contribute to the streamflow well after an event has ceased (Waterfall, 1994; Baglee, 1994). As time progressed the deep-water began to dominate and the pH_c began to rise.

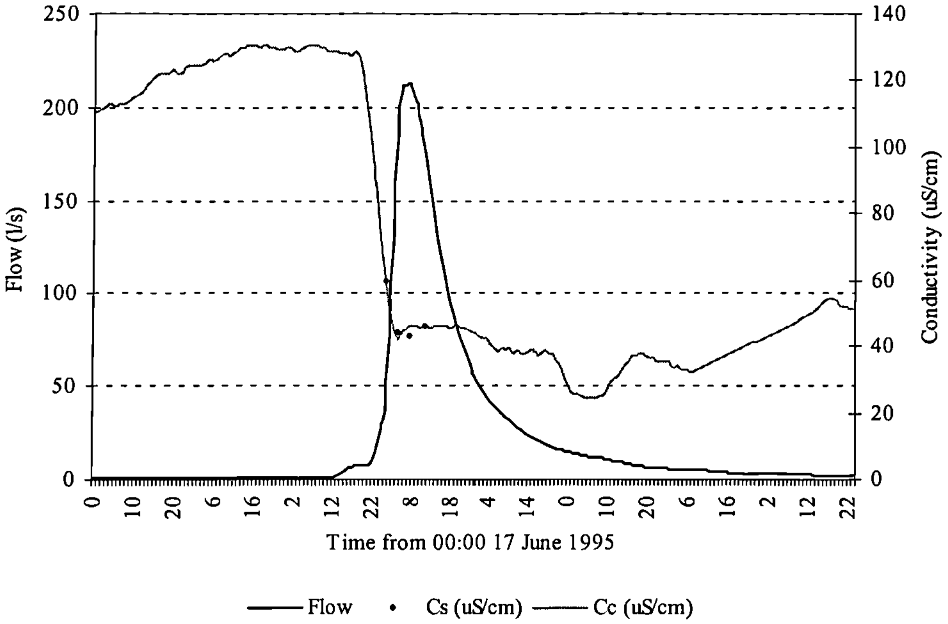
Considering this response in terms of the Coalburn four phase pH response (Table 4.2). On the rising limb the pH_c decreased rapidly as deep-water was diluted by acidic soil and peat sub-catchment water was transmitted along preferential pathways (Phase 1). The catchment shape and slow drainage of acidic soil-water and peat sub-catchment resulted in pH_c minimum after peak flow and a slow recovery (Phase 2 and 3). The stream chemistry only began to recover as the proportional contribution of the deep-water component increased with respect to the slow draining soil and peat sub-catchment water (Phase 3→2→1). The change in the relative contributions from deep, soil, peat and peaty-gley water are different on the rising and recession limbs and this was responsible for the hysterisis observed in the chemical response. In this instance the Coalburn dry antecedent response does not exhibit a recovery phase, which suggests the event was dominated by displacement of pre-event water and no event water reached the stream.

Figure 5.2 Coalburn Event 1 flow, pH and conductivity response

Event 1 flow and pH response



Event 1 flow and conductivity response



Prior to the event the conductivity was high (130 μScm^{-1}) and this slowly decreased during the early part of the event, reflecting the wetting up processes that were operating in the catchment (Figure 5.2). On the rising limb of the hydrograph, the conductivity fell rapidly to a minimum of 42 μScm^{-1}, approximately one hour after the maximum rainfall intensity and three hours prior to the peak flow (Table 5.2).

Under these circumstances the dilution response was expected as the high conductivity deep-water would be diluted by the soil water, as described in the Phase 1 conductivity-flow (Table 4.4). However, if the dilution of deep-water by soil and peat sub-catchment water was the only mechanism causing the response, minimum conductivity would have been expected at either the peak flow or the minimum pH_c (i.e. maximum dilution). This was clearly not the case, with the conductivity reaching a minimum prior to peak flow. At this time the pH_c was 5.82 (pH_s = 5.90) and continuing to fall rapidly. Consequently, the hydrogen ion concentration was increasing and it is hypothesised that the hydrogen ion (and aluminium) began to make a positive contribution to the conductivity and offset the dilution response. Thus, the conductivity stabilised and remained constant as the pH_c fell and the hydrogen ion concentration increased. During the catchment recovery the conductivity fell as the pH_c increased which validates the hypothesised mechanism.

An alternative explanation for this response could be that the conductivity minimum was related to the maximum rainfall intensity and caused by a direct influence of the rainfall, an influence rapidly modified in terms of pH_c but remaining low in conductivity. However, this is unlikely given the low yield of this rainstorm and the low intensities involved, furthermore a conductivity recovery would be expected which was not evident. Thus, the conductivity signal also suggests that pre-event water dominated the event.

The conductivity response observed during Event 1 is a combination of a dilution effect during the early part of the event and then an elevation response due to hydrogen ion/aluminium concentrations later in the event. In terms of the hydrological model, this may represent the switching point between dominance of the well-buffered deep and more acidic soil and peat sub-catchment water. The minimum conductivity representing the exact point at which soil and peat sub-catchment water becomes dominant (i.e. the hydrogen ion contribution is more important than the dilution effect). After this point the dilution of base cations continues, however, in terms of conductivity this is offset by the hydrogen ion and aluminium contributions.

Interestingly during the event, the influence of the 'pool effect' is not apparent (Chapter 2). During periods of base-flow the conductivity in the pool is lower than the conductivity measured in the natural stream. Consequently, with the onset of an event it may have been expected that there would be an initial increase in conductivity if the pool effect were having an influence, this was not observed in this instance.

During the event the calcium and magnesium concentrations decreased (Appendix A), this supports the hypothesis that the deep-water component was diluted by soil and peat sub-catchment water. Potassium and sodium concentrations exhibited a flow-related increase, the patterns of these ions in the soil profiles observed by Hind (1992) and Waterfall (1994) was complex and no straight forward depth relationship was observed. Hind (1992) indicated that the peat soils could give rise to a signature with elevated sodium and potassium and they may account for this pattern during the event.

Alternatively, or additionally, the potassium and sodium response may also reflect the marine origin of the precipitation and a washout effect from the canopy, particularly since potassium can be derived from foliar leaching (Stevens, 1987; Chappell et al., 1990). Indeed, Wake (1994) and Hind (1993) postulated that stemflow was an important component in the hydrochemistry of an event. However, a mechanism by which the canopy signal reaches the stream was not presented. It is thought, in this thesis, that the stemflow could be preferentially routed along the roots to drainage ditches and the catchment outfall. Throughflow may also play a role contributing directly to the drainage ditches but this signal will more dilute than the stemflow (Wake, 1994).

If the stemflow and throughfall were dominating the catchment response then the relationships between the deposition and stream chemistries would be expected to be stronger than observed. This suggests the catchment processes generally dominate but under certain conditions, the canopy signature is detectable in the stream chemistry, these conditions include:

- Long dry antecedent conditions leading to a well conditioned canopy (i.e. distinctive signal).
- Dry soils that lead to cracking around the roots that may improve the hydraulic effectiveness of this pathway.

Aluminium concentrations appeared to peak prior to the minimum pH_c, which was unexpected given the relationship between aluminium and pH. However, this could be explained by the fact that aluminium shows a dilution response at high flows as the concentrations decrease in the upper soil profile at Coalburn (Baglee, 1994) and/or a component of event water could be influencing the response (Soulsby, 1995b). The iron and manganese concentrations showed a similar response resulting from an initial 'flush' of water (rich in these solutes) from within the catchment following the dry period maybe stored in the drainage ditches or from ochreous deposits. This was unlikely to be water from the peaty-gley catchment or movement at depth as these would also be associated with elevated concentrations of calcium and magnesium.

The variations in DOC and colour concentrations were slightly different, which is unusual as the two are closely correlated. The DOC showed a slight increase during the event; this is to be expected as the soil and peat sub-catchment water increase in importance during the event. In contrast, the colour concentration fell initially and then increased as the event continued; this indicates a dilution response and then recovery. This may be from an initial low colour signal from the peaty-gley sub-catchment that is then augmented by the peat sub-catchment and soil water signatures.

5.3.2 Event 2 06 July 1995 DAC / terrestrial / low intensity

The antecedent weather was dry and this was reflected in the antecedent wetness indicators with an API of 11.6mm and a pre-event flow of 0.21 ls^{-1}. These indicators of the catchment's moisture status were low as this event occurred during the 1995 drought.

The antecedent pollution climatology pattern was easterly and anti-cyclonic, there was little rainfall preceding the event. Rainfall chemistry during this period cannot be attributed to either the marine or terrestrial signature, probably reflecting the fact that the rainfall during the event was of marine origin and the relatively small quantity of rainfall with a terrestrial signature would be diluted. The cloud mist sample from that period has a terrestrial signature with low pH and lower concentrations of chloride and sodium and elevated levels on non-marine sulphate. This suggests the catchment was conditioned by cloud mist and dry deposition with a terrestrial signature prior to the event. Initially, the stream chemistry exhibited a deep-water signature, expected during such low flows, with high pH, conductivity, base cations and high buffering capacity. The routine sample taken on 04 July 95 had pH 7.30, conductivity 142 µScm^{-1} and calcium concentration of 1093 µEql^{-1}. The chemistry reflects the fact that Event 2 has one of the lowest flows and driest catchments as a starting point. The hydrochemistry was dominated by the deep-water component from those sustainable sources that have a long residence time at depth (this includes deep-water that may have upwelled through the peat).

Table 5.4 Event 2 06 July 1995

Hydrological Response	**Event 2 06 July 1995**
Antecedent Conditions	
API (mm)	11.6 (05/07)
Pre Event Flow (ls^{-1})	0.21 (06/07 at 0400)
Pre Event pH	7.30
Pre Event Conductivity	142
Prior wind direction	Terrestrial
Event Conditions	
Rainfall Total (mm)	32.4
Maximum intensity (mm hr^{-1})	3.0 (06/07 at 2100) 4.0 (07/07 at 0200)
Total Volume Input (Ml)	48.6
Maximum Flow (ls^{-1})	93.2 (07/07 at 0700) 141 (07/07 at 1300)
Number of peaks	2
Total Flow Output (Ml)	9.11
Runoff ratio (%)	18.7
Storm flow (%)	15.3
Base-flow (%)	3.4
Event wind direction	Frontal
Continuous Hydrochemical Response	
pH$_c$ pulse	No
pH$_c$ Max/Min	7.73/5.08
pH$_c$ fall during event	2.65
Does pH$_c$ lag/coincide/lead	Lag (7 hours)
Conductivity Fall Pulse	No
Conductivity Max/Min	124/64
C$_c$ rise/fall during event	60 (Fall)
Does C$_c$ lag/coincide/lead	Coincide 1st peak.

Solutes			
Calcium (µEql^{-1})	↓	↓	↓
Magnesium (µEql^{-1})	↓	↓	↓
Potassium (µEql^{-1})	↓	↓	↓
Sodium (µEql^{-1})	↓	↓	↓
Chloride (µEql^{-1})	↓	↓	↑
Sulphate (µEql^{-1})	ND	ND	ND
Aluminium (µMoll^{-1})	↑	↑	↓
Iron (µMoll^{-1})	↑	↑	↑
DOC (mgl^{-1})	↑	↓	↓
Colour (mgl^{-1})	↑	↑	↑

Key to solutes

Concentration on rising limb	Concentration at peak flow	Concentration on falling limb

↑ Concentrations increasing.
↓ Concentrations decreasing.
■ No pattern. ND No data.

The rainfall event resulted from the passage of frontal system and the catchment hydrological and hydrochemical response can be seen in Table 5.4, Figure 5.3 and Appendix B.

The total rainfall entering the catchment was relatively low 32.4mm (48.6 Ml) and was low intensity with two peaks (Table 5.4). With the onset of rainfall, the catchment did not immediately respond; it was approximately an hour before the flow increased. This was expected, given that the canopy and soils were dry and a proportion of the rainfall had to make up this deficit.

Hydrograph separation, Table 5.4, indicates that 15 % of the incident rainfall made up the storm-flow component and during the event a total of 19 % of the incident rainfall was discharged at the catchment outfall. Consequently, most of the water entering the catchment was retained/utilised in making up the catchment deficits.

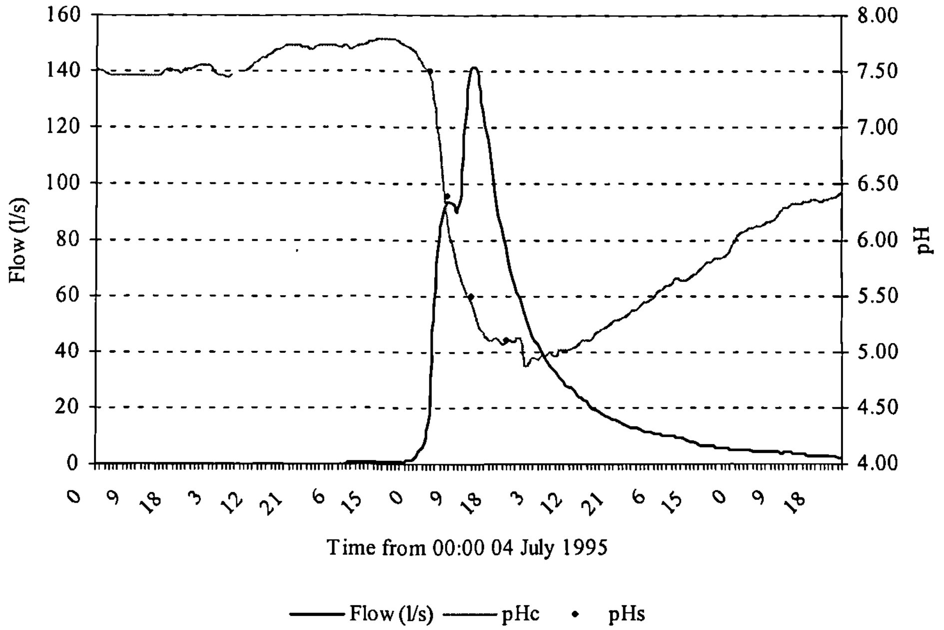
The conditions gradually wetted a dry catchment, and it was several hours before the hydrochemical response was observed, i.e. while the catchment deficits were being replenished the pre-event water continued to dominate. Overall there was a dilution response in the conductivity and an acid episode in the pH reflecting the dilution of the base-flow component by the soil and peat sub-catchment water (Figure 5.3).

The initial pH_c was relatively high (7.73) and, with the onset of rainfall, there was no real change in the pH_c (Figure 5.3). This may be a function of the small volumes of water involved and the comparative volume of the weir pool where the pH_c was measured (i.e. the change is buffered by the weir pool). There was no initial pulse in the pH_c. As flow increased rapidly on the rising limb, the pH_c fell from 7.70 to a minimum of 5.08 lagging the peak flow by seven hours. The pH_c did fall to 4.87, however, this followed a 'jump' in pH for no apparent reason on the recession limb and was considered erroneous. pH_c then slowly recovered.

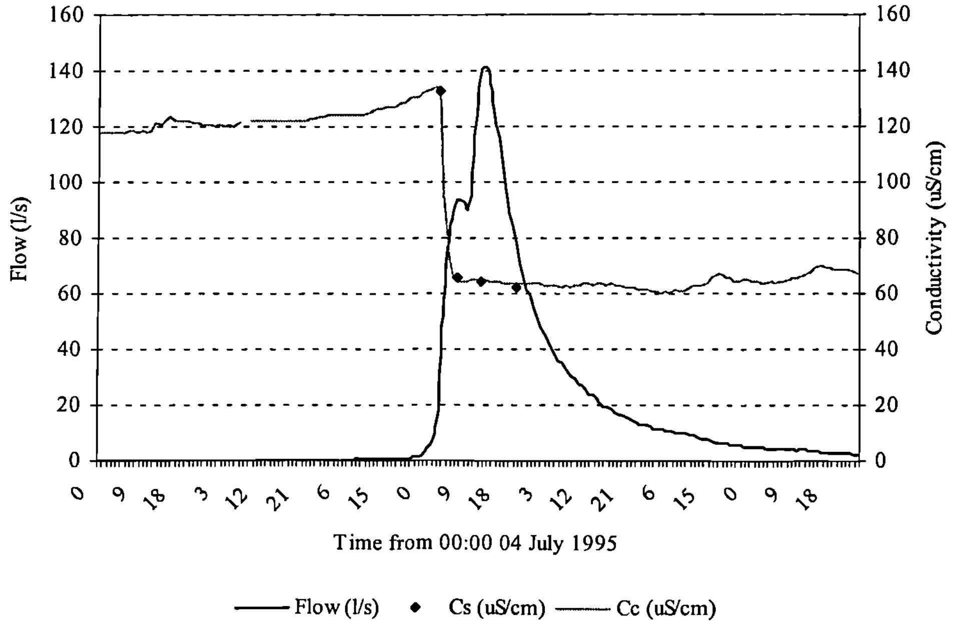
The initial conductivity was high (124 μScm^{-1}), and with the onset of the rainfall there was no change in the conductivity; indeed it increased slightly to a maximum of 135 μScm^{-1} (Figure 5.3). This is likely to be a function of the antecedent dryness and the buffering from the pool. There was no initial pulse in conductivity. As the flows increased rapidly on the rising limb, the conductivity exhibited a dilution response as the deep-water was diluted by the soil and peat sub-catchment water. The minimum conductivity of 64 μScm^{-1} coincided with the first peak in flow. The conductivity then levelled off and there was no

Figure 5.3 Coalburn Event 2 flow, pH and conductivity response

Event 2 flow and pH response



Event 2 flow and conductivity response



further decrease as the flow continued to increase, and showed no sign of recovery until late during the recession limb. The levelling off of the conductivity is probably a response to the increasing concentrations in hydrogen ions that offsets the dilution response and reflects the dominance of soil and peat sub-catchment water.

Both the pH_c and conductivity responses were similar to those observed for Event 1, which suggest similar mechanisms were operating. In this instance, the hydrology and hydrochemistry clearly suggest that pre-event water dominates the event.

The base cations exhibited a dilution response (Appendix B), which was expected for calcium and magnesium, however, it contrasts with the increase in potassium and sodium observed during Event 1. This may be a function of the antecedent conditioning by winds of a terrestrial source that would have been depleted in these ions.

Only chloride data are available for the anions. During the event, chloride showed no definite pattern, although there would appear to be a positive relationship between the intensity of the rainfall and the chloride concentrations. This would imply a component of the rainwater was rapidly reaching the stream during the event; perhaps via the stemflow and throughfall flowpath.

The aluminium concentrations increased with the flow and exhibited a peak close to the maximum flow (similar to the pattern observed for Event 1), implying that comparable processes were operating. The iron response was more complex, increasing to the first peak, decreasing slightly prior to the second peak before increasing on the recession limb. This is a similar pattern to Event 1: attributed to an increased dominance of acidic soil and iron rich peat sub-catchment water.

DOC concentration peaked on the first flow peak and was slightly lower during the remainder of the event. The colour increased during the event, with a maximum on the recession limb coinciding with the pH minimum, suggesting the colour concentrations were related to the volume of soil and peat sub-catchment water making up the stream flow.

It is difficult to compare the Events 1 and 2 as they have different starting points. Event 2 started from a much drier catchment; even though there was more rainfall during Event 2 less was observed as runoff. Event 2 also began with stream chemical characteristics that would permit the buffering of changes caused by an increased soil and peat sub-catchment water. These facts highlight the importance of antecedent wetness in controlling the catchment response. Nevertheless, the basic hydrochemical response of Event 2 is similar to Event 1, despite the differing antecedent catchment conditioning. It was unfortunate that the sulphate data were not available from these events, as these may have given an insight into the effect of catchment conditioning and stemflow signal. Thus, comparison of the two events cannot conclusively prove or disprove a difference between the catchment responses resulting from catchment conditioning.

Table 5.5 Event 3 03 July 1996

Hydrological Response	**Event 3 03 July 1996**
Antecedent Conditions	
API (mm)	28.1 (02/07)
Pre Event Flow (ls^{-1})	2.77 (03/07 at 0300)
Pre Event pH	6.95
Pre Event Conductivity	79
Prior wind direction	Mixed
Event Conditions	
Rainfall Total (mm)	35.0
Maximum intensity (mm hr^{-1})	5.6 (04/07 1300)
Total Volume Input (Ml)	52.5
Maximum Flow (ls^{-1})	217.8 (04/07 1700)
Number of peaks	3
Total Flow Output (Ml)	14.6
Runoff ratio (%)	27.8
Storm flow (%)	21.3
Base-flow (%)	6.54
Event wind direction	Cyclonic
Continuous Hydrochemical Response	
pH$_c$ pulse	No
pH$_c$ Max/Min	6.95/4.52
pH$_c$ fall during event	2.43
Does pH$_c$ lag/coincide/lead	Lag (3 hours)
Conductivity Fall Pulse	No
Conductivity Max/Min	79/53
C$_c$ rise/fall during event	26 (fall)
Does C$_c$ lag/coincide/lead	Complex – see text

Solutes			
Calcium (μEql^{-1})	↓	↓	↓
Magnesium (μEql^{-1})	↓	↓	↓
Potassium (μEql^{-1})	↑	↑	↑
Sodium (μEql^{-1})	↑	↓	↑
Chloride (μEql^{-1})	↑	↓	↑
Sulphate (μEql^{-1})	↑	↑	↓
Aluminium (μMoll^{-1})	↑	↓	↑
Iron (μMoll^{-1})	↑	↓	↑
DOC (mgl^{-1})	↑	↓	↑
Colour (mgl^{-1})	↑	↓	↑

Key to solutes

Concentration on rising limb	Concentration at peak flow	Concentration on falling limb

↑ Concentrations increasing.
↓ Concentrations decreasing.
■ No pattern.

5.3.3 Event 3 03 July 1996 DAC / marine / normal to intense

The antecedent weather was dry and this was reflected in the antecedent wetness indicators with an API of 28.1mm and pre event flow of 2.77 ls^{-1}. While the antecedent wetness indicators were low, the flow was an order of magnitude larger than the previous events examined as it followed a series of earlier events.

Samples of the rainfall and cloud mist on 02 and 18 July revealed the antecedent pollution climatology could not be attributed to either the terrestrial or marine signature, although marine airmasses dominated the weather for the previous week.

The stream chemistry had high conductivity, pH and base cations, however, these were not as elevated as in Events 1 and 2. This reflects the higher flow at the onset of Event 3 and the streamflow would be a combination of the deep and soil water components, indicating the importance of the antecedent wetness.

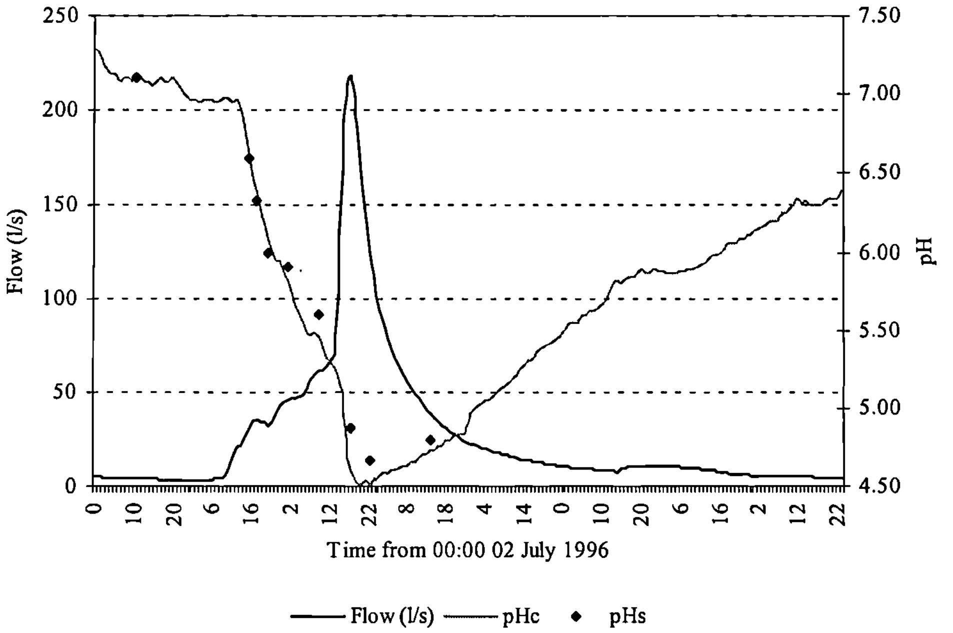
The rainfall event resulted from the passage of a frontal system and the catchment hydrological and hydrochemical response can be seen in Table 5.5, Figure 5.4 and Appendix C. With the onset of rainfall, the catchment does not immediately respond; it was approximately two hours before the flow increased. This was expected given the canopy and soils were dry and a proportion of the rainfall had to make up the deficits prior to contributing to streamflow. The rainfall fell in three distinct phases, as follows:

Date	Time Start	Time Finish	Total Rainfall (mm)	Maximum Intensity (mm hr^{-1})	Time
03 July	0100	1300	13.4	2.8	0800
03 July	1900	2200	5.00	3.4	2000
04 July	0100	05/07 at 2200	16.6	5.6	1300 04/07

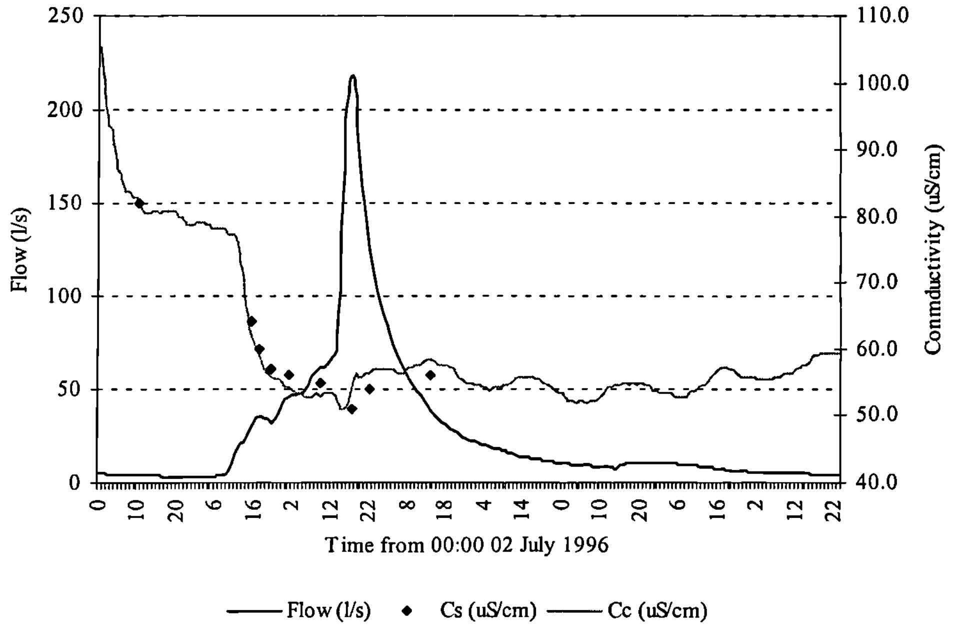
The complexity of this input signal is reflected in the distinctive hydrograph (Figure 5.4). The first rainfall resulted in relatively slow increase in flow to a peak of 35 ls^{-1}. The flow then decreased and the second rainfall resulted in flows rising steadily reflecting the low intensity of the rainfall. This was followed immediately by the third rainfall of low intensity and the flow increased relatively slowly. Then 5.6mm fell on the catchment in one hour and this caused the flow to increase from 70 ls^{-1} to 218 ls^{-1} four hours after the maximum intensity. The rainfall then ceased and the flow receded.

Figure 5.4 Coalburn Event 3 flow, pH and conductivity response

Event 3 flow and pH response



Event 3 flow and conductivity response



Hydrograph separation (Table 5.5) indicates that 21 % of the incident rainfall made up the storm flow component and during the event a total of 28 % of the incident rainfall was discharged at the catchment outfall. Consequently, most of the water entering the catchment was retained/utilised in making up the catchment deficits.

The initial pH_c was 6.95 and, with the onset of rainfall there was no major change in the pH_c for twelve hours, and there was no initial pulse in the pH_c (Figure 5.4). Event 3 was characterised by the relatively slow rise in flow, and this is reflected in the slow pH_c fall. This confirms the hypothesis that the rate of change in pH_c is inversely proportional to the flow, reflecting the relative speed at which the soil and peat sub-catchment water becomes dominant over the deep and peaty-gley water. At 1200 (04 July) the pH_c was 5.29, prior to the intense rainfall and when the flow began to increase rapidly the pH_c fell to a minimum of 4.52, which lagged peak flow by three hours. The stream pH_c then began to recover.

The initial conductivity was 79 μScm^{-1} and with the onset of rainfall there was no initial conductivity pulse (Figure 5.4). The conductivity exhibited a dilution response and fell to a minimum of 53 μScm^{-1} where upon the conductivity levels off, as observed in the Events 1 and 2. During and immediately following the maximum rainfall intensity, the conductivity shows a brief, slight dilution response (which suggest the rainfall had a direct influence on the stream conductivity under these conditions). This is consistent with the hypothesis (Chapter 4) that rainfall can be rapidly delivered to the stream during periods of intensive rainfall, or when the catchment is saturated. Thus, while the event was dominated by pre-event water, there was a brief delivery of event water to the stream following intense rainfall. However, this only affected the conductivity; the pH was modified by the catchment processes by the time it reached the catchment outfall.

Following the intense rainfall, the conductivity increased as its diluting effects diminished. Despite the increase in flow and fall in pH_c the conductivity remained approximately constant as observed in the previous Events 1 and 2. The pH_c and conductivity then began to slowly recover.

Event 3 highlights the difference in the pH_c and conductivity response, with the pH_c falling at a slower rate than the conductivity, which is the same in Events 1 and 2. It has been hypothesised that the conductivity and pH_c responses reflect an increase in the soil and peat sub-catchment water diluting the deep and peaty-gley sub-catchment water. However, if this were the case, the rates of change would be alike and the responses would have been synchronous. The explanation for the non-synchronous response of the pH_c and conductivity is the relationship of conductivity and the hydrogen ion concentration discussed in Chapter 4. Similarly the characteristics of the rate of change can be attributed to the conductivity measurement; at high pH the bicarbonate ion begins to contribute disproportionately to the conductivity (Figure 4.6). Consequently, the dilution of the deep-water by soil and peat sub-catchment water results in a rapid change in conductivity for a relatively small change in pH; at intermediate pH values larger changes in pH are required to change conductivity; while at lower pH the conductivity begins to increase more for changes in pH. The same applies for the differences in the conductivity and pH_c recoveries.

Eight samples were taken throughout Event 3 (Appendix C). Calcium and magnesium concentrations exhibited the expected dilution response during the event; however, the sampling intensity was such that any direct rainfall effect was not visible in the results. Potassium exhibited increased concentrations during the event and particularly following the intensive rainfall/peak flow, this could reflect potassium derived from the canopy sources (foliar leaching) being rapidly delivered to the catchment outfall by the direct rainfall influence.

The sodium concentrations were slightly elevated during the event, suggesting the marine influence dominated; however, the response pattern was complex. Initially, the rainfall resulted in an increase in sodium concentrations similar to Event 1. However, following the 5.6mm hr^{-1} rainfall burst, there was a transitory decrease in the sodium concentrations observed in the stream, before the concentrations increased. The pattern is consistent with the conductivity response and the view that catchment processes dominated for most of this event, except following the intense rainfall when an element of event water was delivered to the catchment outfall. The event water must have had a lower concentration of sodium than pre-event water; this would be expected as the highest concentrations of solutes in rainfall occur at the beginning of a storm (Cresser and Edwards, 1987) and the solutes would have been washed from the canopy.

During the event, the chloride concentrations were lower than the sample taken a few days prior to the event. During the early phases the chloride concentration increased, lagging the hydrograph slightly. The chloride concentrations then decreased following the intensive burst of rainfall, which is consistent with the view that dilution by event water occurs. Sulphate concentration increased during the rising limb of the event, reached its maximum at peak flow and then decreased on the recession limb.

The aluminium concentrations increased during the rising limb with a maximum prior to the intensive rain period, after which the concentrations decreased. On the recession limb aluminium concentrations increased slightly. The iron and manganese concentrations exhibited a similar pattern except there is no recovery on the falling limb.

The DOC and colour concentrations also had a similar response to aluminium, although slightly more pronounced. During the rising limb, the increasing concentrations of the DOC and colour reflected the increasing contribution of water from the soil and peat sub-catchment that are enriched with respect these solutes. The decrease around the intense rainfall and peak flow probably reflected the event water influence that would be DOC and colour depleted, while on the recession limb the soil and peat sub-catchment water became important sources of these solutes again and their concentrations increased.

5.3.4 Event 4 06 July 1994 DAC / terrestrial / high intensity

The antecedent weather was dry and this is reflected in the antecedent wetness indicators with an API of 19.4 mm and pre-event flow of 1.05 ls^{-1}. The antecedent weather was anticyclonic, the wind direction from the south-east sector. The rainfall chemistry during the period 14 June to 04 July 1994 reflected the changeable weather during that period and the chemistry was a mix of the marine and terrestrial signatures. The rainfall pH was 5.50, sulphate was slightly elevated above normal 60 μEql^{-1} and sodium is slightly lower at 39 μEql^{-1}. This suggests that there could have been some conditioning of the catchment by the terrestrial signature through the dry deposition. Initially, the stream chemistry had high conductivity, pH and base cation concentrations, suggesting that the deep-water signature was dominating the stream chemistry prior to the event.

The event resulted from a thunderstorm and the catchment's hydrological and hydrochemical response can be seen in Table 5.6, Figure 5.5 and Appendix D. During the thunderstorm, 16.4mm of rain fell in 6 hours, the first three hours being the most intense

(6.0mm, 7.0mm and 2.6mm respectively). The thunderstorm resulted in the flow increasing from 1 ls^{-1} to 93 ls^{-1} in five hours. The quick hydrological response may have resulted from drying of the catchment soils causing some of the peat areas to become hydrophobic and peaty-gley to crack (especially around tree roots). This may have promoted rapid runoff and a greater contribution of event water to the storm event than would have been observed if the rainfall intensity was less (Soulsby, 1994).

Hydrograph separation (Table 5.6) indicates that 13% of the rainfall made up the storm flow component of the event and a total of 18% of the rainfall was discharged at the catchment outfall during this period. This suggests, despite the intensity of the event, that much of the rainfall made up the catchment deficits.

There was no significant pH_c or conductivity pulse and both fell rapidly reacting to the increased flow (Figure 5.5). Their response lagged the hydrograph, with pH_c lagging the most. The pH_c depression during the event was reasonably large for the flow increase (7.21 to 5.91), although the minimum pH

Table 5.6 Event 4 06 July 1994

Hydrological Response	**Event 4** **06 July 1994**
Antecedent Conditions	
API (mm)	19.4 (05/07)
Pre Event Flow (ls^{-1})	1.05 (06/07 1700)
Pre Event pH	7.21
Pre Event Conductivity	60
Prior wind direction	Easterly sectors
Event Conditions	
Rainfall Total (mm)	16.4
Maximum intensity (mm hr^{-1})	7.00
Total Volume Input (Ml)	24.6
Maximum Flow (ls^{-1})	93.22
Number of peaks	1
Total Flow Output (Ml)	4.32
Runoff ratio (%)	17.5
Storm flow (%)	13.0
Base-flow (%)	4.5
Event wind direction	Easterly sectors
Continuous Hydrochemical Response	
pH_c pulse	No
pH_c Max/Min	7.21/5.91
pH_c fall during event	1.30
Does pH_c lag/coincide/lead	Lag (7 hours)
Conductivity Fall Pulse	No
Conductivity Max/Min	60/35.4
C_c rise/fall during event	Fall (24.6)
Does C_c lag/coincide/lead	Lag (2 Hours)

Solutes			
Calcium (μEql^{-1})	ND	ND	ND
Magnesium (μEql^{-1})	ND	ND	ND
Potassium (μEql^{-1})	ND	ND	ND
Sodium (μEql^{-1})	ND	ND	ND
Chloride (μEql^{-1})	ND	ND	ND
Sulphate (μEql^{-1})	ND	ND	ND
Aluminium ($\mu Moll^{-1}$)	ND	ND	ND
Iron ($\mu Moll^{-1}$)	ND	ND	ND
DOC (mgl^{-1})	ND	ND	ND
Colour (mgl^{-1})	ND	ND	ND

Key to solutes

Concentration on rising limb	Concentration at peak flow	Concentration on falling limb

↑ Concentrations increasing.
↓ Concentrations decreasing.
■ No pattern.
ND No data.

was not exceptionally acidic. Given the speed and intensity of the catchment response, it may be plausible that there was a dominance of event water (infiltration/vertical drainage served to make up the catchment deficit).

If event water dominated then the acidity was unlikely to originate from the soil and peat sub-catchment water, as the contact time with these zones would have been short. The acidity could be explained by catchment conditioning (Davies et al., 1992). During the antecedent dry period winds were from an easterly to south easterly track and this led to deposition of acid ions. An accumulation of acidic ions on the canopy was then washed off during event, increasing the acidity of the net precipitation. The acidity was then rapidly transferred to the stream (with little buffering) where (combined with the dilution of base cations) it produced the observed pH depression.

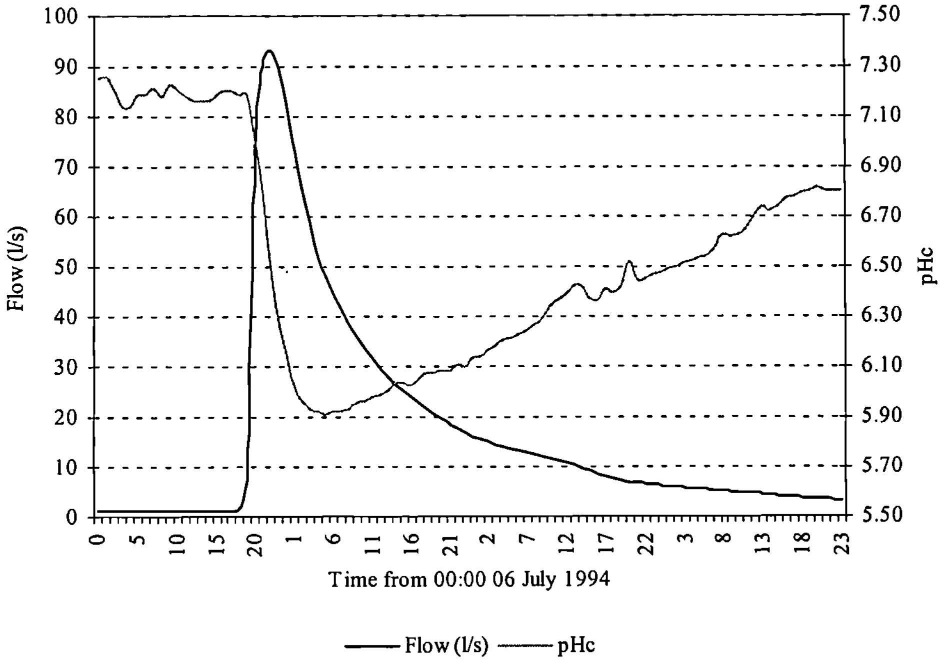
The conductivity response during the event showed a classic dilution response (Figure 5.5). There are two possible explanations, depending upon the chosen hypothesis regarding the importance of event water, either:

> The dilution effect was rainfall driven by the intense rainfall promoting lateral drainage to the stream; this low conductivity and acid anion enriched solution then diluted the well buffered streamwater to cause the observed response.
>
> **or**
>
> The dilution effect was a soil-driven mechanism and reflects the dilution of the deep-water component by soil and peat sub-catchment water; the dilution of bicarbonate has an important influence on conductivity in the pH range (7.50-5.50) observed during this event

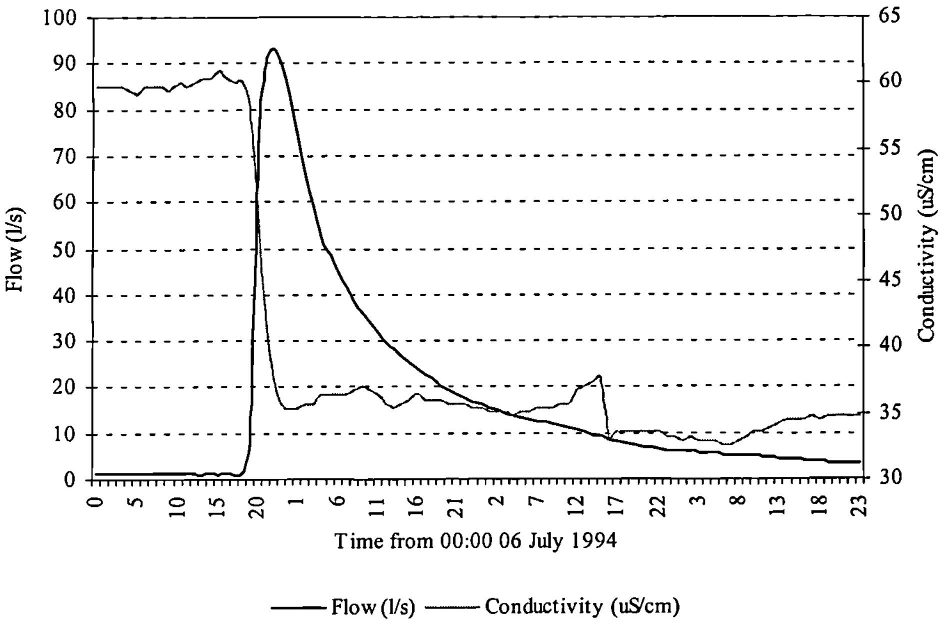
If the event water theory were correct, it would be expected that the pH_c and conductivity response would be in phase with the flow response and there would be an immediate recovery with cessation of the rain. However, the pH_c lagged the peak flow by seven hours and the conductivity lagged by two hours and the recoveries were extended as per the 'regular' event. The pH_c response would appear to be dominated by the soil and peat sub-catchment water as the lag and recovery is typical of what has been observed in other responses (Events 1, 2 and 3). The conductivity response was also driven by the soil and peat sub-catchment water, as the recovery was slow. However, the lag time between peak flow and minimum conductivity was only two hours, which suggest that there could have been a component of event water. The other events have shown a direct conductivity/pH response to rainfall intensities of this order and no such response is observed; in fact, the conductivity and pH responses are smooth/regular. This would suggest the response was primarily driven by the pre-event water deep/soil water component being diluted by soil water rather than event water. The fact that only 13% of the rainfall entering the catchment contributed to the storm event implies much of the rainfall was retained in the catchment despite the rainfall intensity. Indeed the cracking of the peaty-gley soils may have facilitated quicker vertical movement of the rainfall.

Figure 5.5 Coalburn Event 4 flow, pH and conductivity response

Event 4 flow and pH response



Event 4 flow and conductivity response



5.3.5 Event 5 23 April 1996 DAC / terrestrial / normal

The antecedent weather was dry and this was reflected in the antecedent wetness indicators with an API of 36.7mm and pre-event flow of 8.76 ls^{-1}. While the antecedent wetness indicators were low, the flow and API were greater compared to the other events that have been examined.

The antecedent wind direction was from the easterly sectors for most of the previous month and during the event this changed to the south-westerly sector. This was reflected in the rainfall and cloud mist data collected during this period; these had pH of 4.4 and 4.3 respectively. The lack of volume meant the rainfall analysis was incomplete. However, ammonium concentrations were elevated to 50 μEql^{-1}, indicative of the terrestrial signature. The cloud mist similarly showed elevated concentrations of ammonium and sulphate (415 and 706 μEql^{-1} respectively). These results suggest the catchment was conditioned by the terrestrial chemical signature and the lack of rainfall during the antecedent period suggests that dry deposition would have played an important role.

Table 5.7 Event 5 23 April 1996

Hydrological Response	**Event 5 23 April 1996**
Antecedent Conditions	
API (mm)	36.7 (23/04)
Pre Event Flow (ls^{-1})	8.76 (23/04 at 0400)
Pre Event pH	6.17
Pre Event Conductivity	70
Prior wind direction	Easterly
Event Conditions	
Rainfall Total (mm)	28.6
Maximum intensity ($mm\ hr^{-1}$)	3.6 (23/04 at 0600)
Total Volume Input (Ml)	42.9
Maximum Flow (ls^{-1})	158 (23/04 at 1200) 124 (24/04 at 0700) 116 (24/04 at 1400) 132 (24/04 at 2100)
Number of peaks	4
Total Flow Output (Ml)	22.2
Runoff ratio (%)	52.0
Storm flow (%)	35.0
Base-flow (%)	18.0
Event wind direction	Cyclonic
Continuous Hydrochemical Response	
pH_c pulse	On later peaks
pH_c Max/Min	6.16/4.32
pH_c fall during event	1.8
Does pH_c lag/coincide/lead	Lag
Conductivity Fall Pulse	On later peaks
Conductivity Max/Min	Complex see text
C_c rise/fall during event	Complex see text.
Does C_c lag/coincide/lead	Lag.

Solutes			
Calcium (μEql^{-1})	↓	↓	↑
Magnesium (μEql^{-1})	↑	↑	↓
Potassium (μEql^{-1})	↓	↑	↓
Sodium (μEql^{-1})	↓	↑	↓
Chloride (μEql^{-1})	↑	↓	↑
Sulphate (μEql^{-1})	↑	↓	↑
Aluminium ($\mu Moll^{-1}$)	↑	↑	↓
Iron ($\mu Moll^{-1}$)	↑	↑	■
DOC (mgl^{-1})	↑	↑	■
Colour (mgl^{-1})	↑	↑	■

Key to solutes

Concentration on rising limb	Concentration at peak flow	Concentration on falling limb

↑ Concentrations increasing.
↓ Concentrations decreasing.
■ No pattern. ND No data.

The stream chemistry had high conductivity, pH and base cation concentrations prior to the event. However, these were not as elevated as the previous events, reflecting the higher initial flow of Event 5. Consequently, the streamflow would already have been a mixture of the deep and soil and peat sub-catchment water components, indicating the importance of the antecedent wetness dynamic.

The rainfall event resulted from the passage of a frontal system and the catchment hydrological and hydrochemical response can be seen in Table 5.7, Figure 5.6 and Appendix E. The total rainfall entering the catchment was 28.6 mm (42.9 Ml). With the onset of rainfall, the catchment does not immediately respond. It was approximately two hours (1.4 mm) before the flow increased, which was expected as a proportion of the rainfall had to make up these deficits prior to contributing to streamflow. The rainfall fell in three distinct phases, as follows:

Date	Time Start	Time Finish	Total Rainfall (mm)	Maximum Intensity (mm hr^{-1})	Time
23 April	0200	1000	15.4	3.6	0600
23 April	1900	0300	6.6	2.6	0100
24 April	1000	1700	6.6	2.4	1700

The complexity of the input signal is reflected in the hydrograph that had four peaks (Table 5.7; Figure 5.6; Appendix E). Hydrograph separation (Table 5.7), indicates that 35% of the incident rainfall made up the storm flow component and during the event a total of 52% of the incident rainfall was discharged at the catchment outfall. These quantities of flow are greater than the other DAC events examined, reflecting the elevated antecedent storage. Nevertheless, the catchment retained nearly half of the water entering it during the event.

The catchment was partially saturated by previous events, and was therefore more 'sensitive' to this event in terms of hydrology and chemistry, however, it was still several hours before the hydrochemical response was observed. During this time, the catchment deficits were replenished and the pre-event water continued to dominate.

The initial pH_c was 6.16 and, with the onset of rainfall there was no major change in the pH_c for five hours, and there was no initial pulse (Figure 5.6). As the flow continued to increase rapidly the pH_c fell rapidly to 4.48, lagging the peak flow by five hours. This response was due to the relative speed at which the soil and peat sub-catchment water becomes dominant over the deep-water. The flow then recovered slightly, however, the pH_c remained constant, which suggests that water of the same chemistry continued to contribute, despite the flow decrease, and delayed the catchment recovery. This implies the soil/peat water continued to dominate on the recession, which was expected given the hydraulic conductivity of the peat.

During the second rainfall, the pH_c was already depressed to 4.48, and there was an initial transient increase in the pH_c, which was expected (see later). Following this pH_c fell slowly during this period to pH_c 4.40, despite a relatively large increase in flow; this may reflect that the acidic soil and peat sub-catchment water were already a significant component of flow at the catchment outfall. Consequently, major changes in the pH/flow relationship (Phase 3) had occurred and the soil and peat sub-catchment water was dominating the catchment response (i.e. the catchment was not sensitive to rainfall inputs as the pH_c only decreases by a small amount). The streamflow then decreased slightly, although there was no corresponding recovery in pH_c.

During the third rainfall, the pH_c was already depressed to 4.40 and there was an initial transient increase in pH_c. Following this, the pH_c fell to a minimum of 4.32, which was low for this flow rate. This trough lagged the final peak flow by five hours: consistent with the observation that the most acidic water do not contribute until the recession limb. After this point, the pH_c began to recover slowly.

During the second and third phases of rainfall there appeared to be a positive relationship between the rainfall intensity and pH_c. The pH_c increased slightly following intense periods of rainfall, this suggest a pulse of high pH_c water was reaching the catchment outfall, this could occur due to:

1. The south-east peaty gley sub-catchment is located close to the catchment outfall and has a high pH (and conductivity) signature. Consequently, a pulse from this peaty-gley sub-catchment could be mixing with the other catchment water, its higher pH causing a slight increase.

2. An input of higher pH event water through a direct influence of rainfall increasing the stream pH.

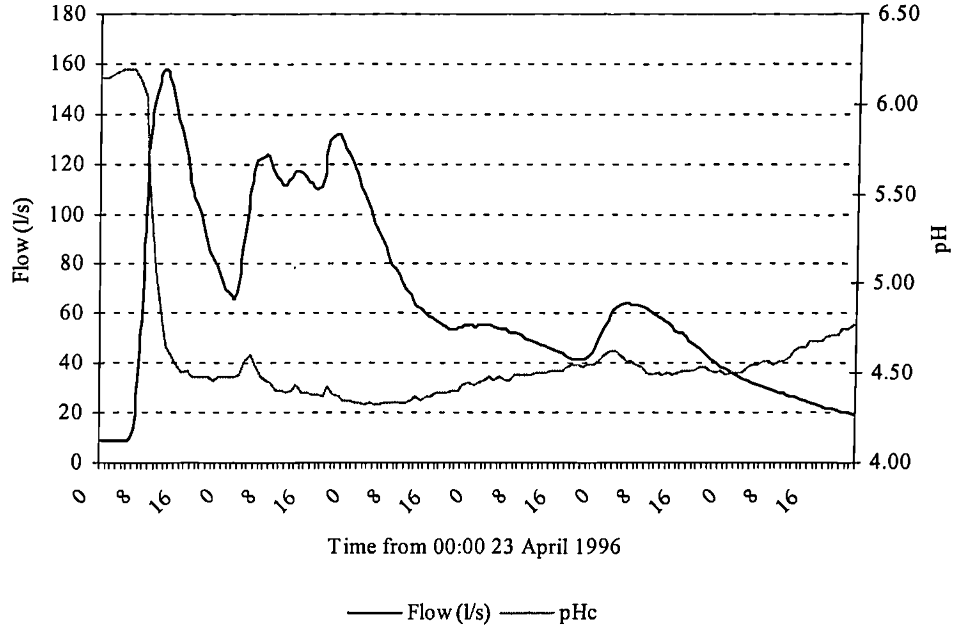
Given the small changes involved both mechanisms are plausible, however, previous evidence presented here has demonstrated the rainfall signal is rapidly modified in terms of pH by the catchment processes.

The pre-event conductivity of 70 μScm^{-1} suggests that the catchment output was a mix of soil and deep-water. During the early part of the event the flow rapidly increased and this was mirrored by the conductivity (Figure 5.6), as the deep-water was rapidly diluted by soil water and this reached a minimum an hour before peak flow (64 μScm^{-1}). Uncharacteristically for a dry antecedent condition event, the conductivity then began to increase rapidly. This was almost certainly driven by the continuing fall in pH and the increase in hydrogen ion (and aluminium) concentrations that contributed to the conductivity. The conductivity reached a maximum at the minimum pH_c, and as such this event is a composite of the dry and wet antecedent conditions response and reflects the fact that classifying the events does have limitations.

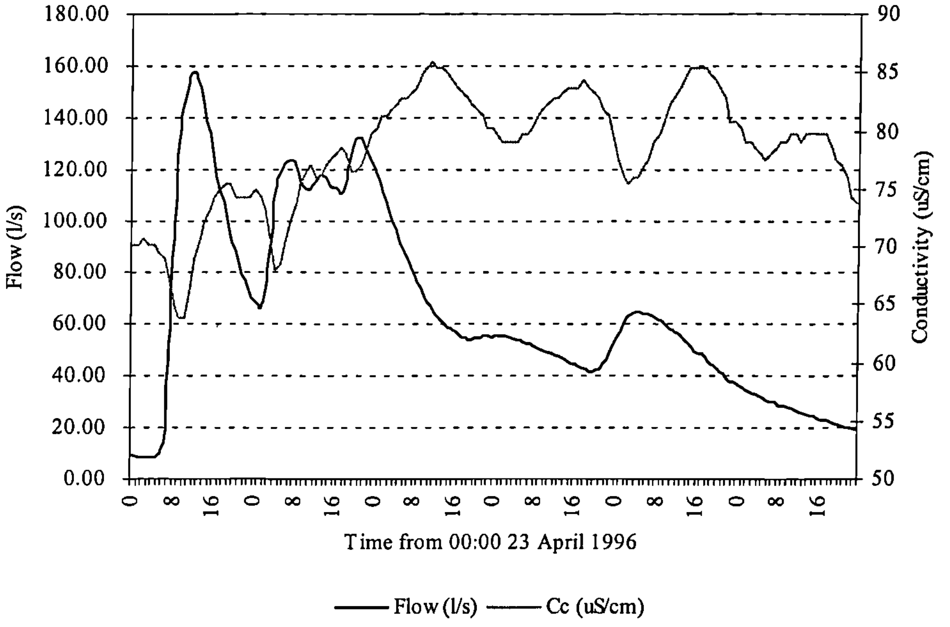
During the second rainfall, the conductivity exhibited an initial transient decrease in the conductivity (slight dilution) that was synchronous with pH_c pulse. The initial pulse is a signature of the wet antecedent conditions response and was expected in this instance, a discussion on the mechanism causing the response is covered later. The conductivity then began to rise slightly. Finally, during the third rainfall the response exhibited the initial pulse and a slight increase. As the flow receded, the conductivity continued to rise as the pH_c fell to a minimum, which is consistent with the hydrogen (and other) ions driving the conductivity response. The conductivity then began to recover as the hydrogen ion concentration increased.

Figure 5.6 Coalburn Event 5 flow, pH and conductivity response

Event 5 flow and pH response



Event 5 flow and conductivity response



The complexity of the hydrological response is reflected in the other chemical solute responses (Appendix E), consequently with only a few samples it is difficult to back-cast and tease out the processes and flowpaths operating from these data.

The aluminium concentrations showed a slight increase with the flow; however, given the acidity of the event higher concentrations were expected as was a stronger relationship with flow. This may suggest that an element of the acidity is derived from the dry deposition washoff (depleted in aluminium but acidic) during the early phase of the event, rather than catchment sources.

Iron, colour and DOC concentrations exhibited a similar pattern that basically reflects the dominance of soil and peat sub-catchment water during various phases of the event.

Chloride and sulphate concentrations exhibit similar patterns that suggests that a washout process dominated the catchment chemistry initially (i.e. that catchment conditioning is important), while later during the event catchment processes dominate.

Calcium concentrations exhibited a dilution response during the early part of the event, as expected. However, on the subsequent peaks the calcium concentrations increased slightly prior to the increase in pH_c. This may be indicative of the rapid response of the peaty-gley sub-catchment (postulated earlier), as this will have an elevated calcium concentration signature.

The magnesium concentration increased massively at the first peak flow increase and then decreased to a minimum at the beginning of the second event. The concentration then followed a basic pattern of increasing at the peak flows and decreasing between them. This contrasts the calcium pattern (to which magnesium values are usually correlated) and may reflect that magnesium can also be derived from marine sources (Chapter 3).

5.3.6 Dry antecedent condition events: summary and discussion

The Events 1 to 4 exhibited a remarkably consistent response to a small to medium rainfall event ending a period of antecedent dry conditions. Essentially, the classification restricted the antecedent and event conditions to the Phase 1 of the conductivity-flow relationship (Table 4.4) and Phases 1 and 2 for the pH-flow relationship (Table 4.2). During these phases, the dominant process that controls the catchment hydrochemical response is the dilution of deep and peaty-gley sub-catchment water by soil and peat sub-catchment water, resulting in the pattern of a decrease in conductivity, pH and base cation concentrations.

The typical response has flow leading the minimum pH_c and conductivity, and a slow hydrochemical recovery following an event. This suggests that pre-event water dominates; if event water were the cause of the response the minimum values of pH_c and conductivity would by synchronous with the peak flow. The lag reflects the time the catchment takes to wet up and the maximum soil water contribution to occur. Furthermore the catchment shape and soil distribution implies the more acidic peat sub-catchment do not contribute until later during an event, and their relative contribution (i.e. they cover 75% of catchment) will drown out other signals. The hydrochemical response is consistent with the hydrological response that indicates that most of the rain entering the catchment is retained to make up the moisture deficits. The slow recovery reflects the low hydraulic conductivity of the peat that continues to contribute well after an event.

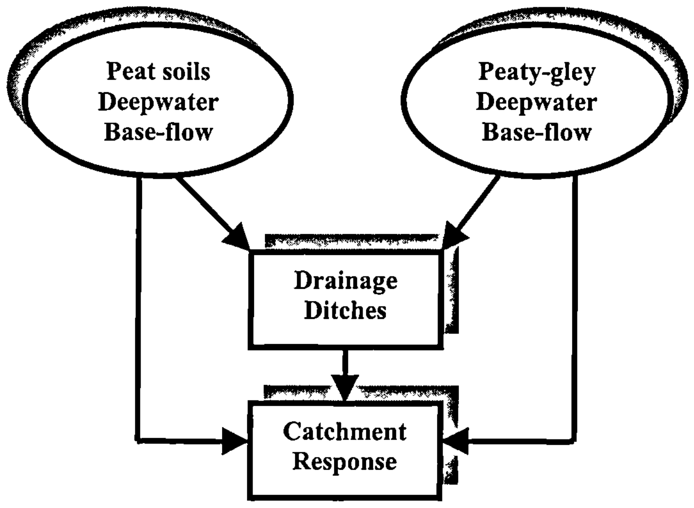
While a DAC event hydrochemical response was generally driven by pre-event water, a period of intense rainfall in Event 3 resulted in a component of event water reaching the stream. This event water mixed with the pre-event water and resulted in a decrease in conductivity reflecting the influence of the low conductivity rainfall. However, there was no such response in pH_c, which can be accounted for by rapid modification of the pH signal by catchment processes. The improved drainage network provides the conduit to rapidly transfer the intense rainfall to the catchment outfall, and the artificial drainage would appear to still play a fundamental role in the Coalburn hydrochemical response even after 27 years. This confirms the hypothesis that during periods of intense rainfall, event water may influence the stream chemistry, a concept first put forward in Chapter 4.

The catchment chemical gradients, i.e. natural acidity from the peat and base cation dilution by the soil and peat sub-catchment water, are of sufficient magnitude to account for the acid event. However, analysis of Events 1 to 4 indicates that antecedent conditioning may play a role in the hydrochemical response. There was evidence that canopy washout could reach the stream by throughfall falling directly into the drainage ditches and the stemflow being rapidly routed to the drainage ditches along the tree roots. This process does not occur under normal conditions, however, it is likely to be enhanced by long dry antecedent conditions leading to a well conditioned canopy (i.e. distinctive signal) and dry soils that improve the hydraulic effectiveness of this pathway (i.e. cracking around roots).

Where the antecedent catchment saturation is higher or a reasonably large event ends a dry period, the hydrochemical response is no longer constrained to the Phase 1 of the conductivity-flow and pH-flow relationship. Consequently, the event may initially respond in a DAC manner, however, as the event progresses it moves into the other phases of the pH/conductivity-flow relationship and is characterised by the WAC event response (discussed below). A good example of this composite response was Event 5.

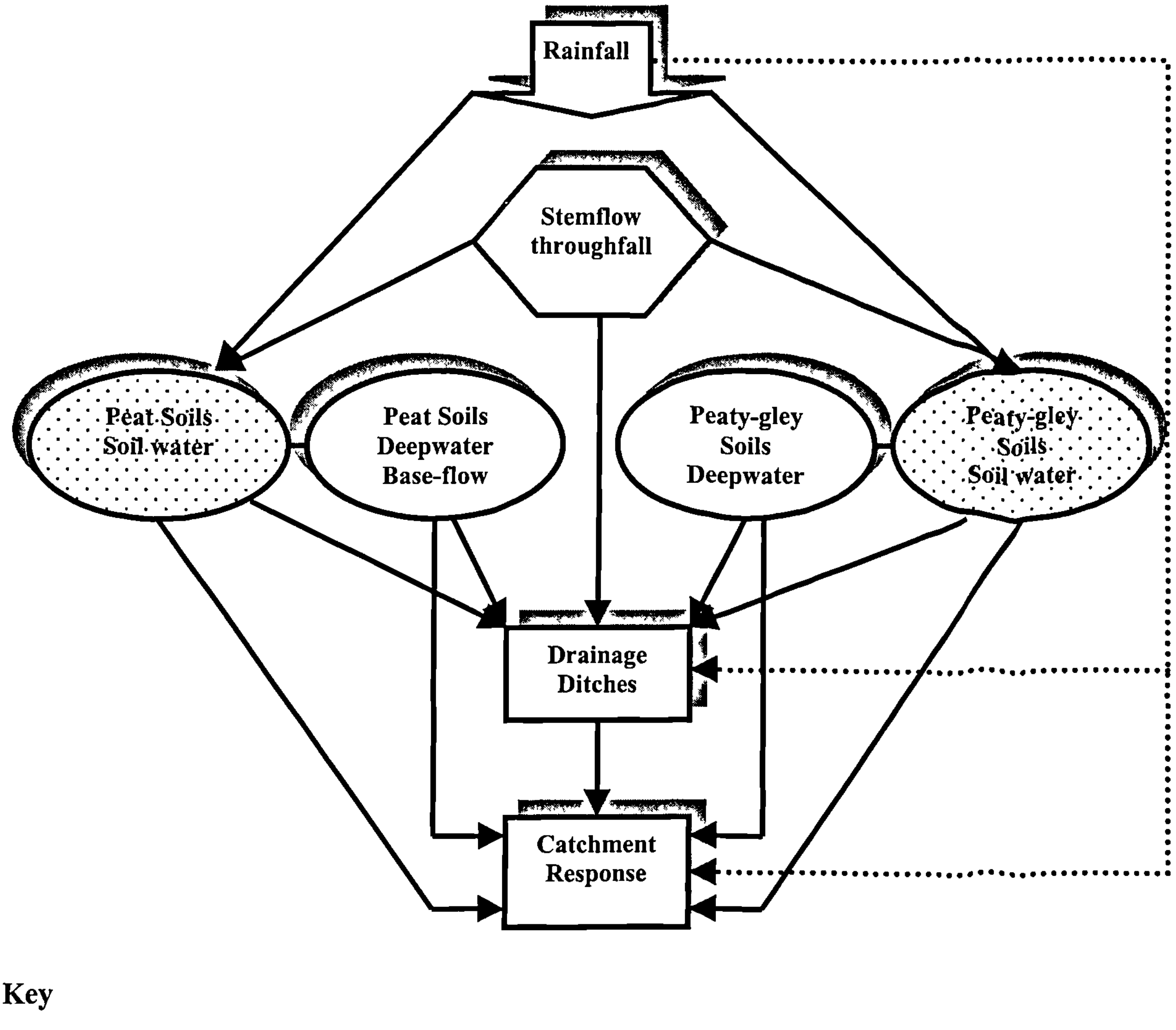
In terms of the Coalburn runoff model the starting point for a dry antecedent event is with the streamflow being derived from the deep-water components of the peat and peaty-gley sub-catchments (Figure 5.7).

Figure 5.7 Coalburn runoff model dry antececdent conditions: event starting point



In response to rainfall on the catchment the active flowpaths become more complex (Figure 5.8). When rainfall enters the catchment, it can be partitioned to the canopy or in the unplanted areas. The stemflow and throughfall then contribute to the peat and peaty-gley upper soil waters, some of which move vertically to the deep-water components. In events with very dry antecedent conditions (and the canopy has a distinctive chemical signature) the stemflow and throughfall signature can be rapidly routed to the drainage ditches and catchment outfall.

Figure 5.8 Coalburn runoff model dry antececdent conditions: event flowpaths



Key

•••••••••••••• Event water component

Shaded area = primary source.

The bulk of the catchments hydrological and hydrochemical response, during a dry antecedent event, was explained by an increased volume of water being delivered from the soil water and peat sub-catchment components (shaded in Figure 5.8). However, under intense rainfall a 'direct' rainfall component was seen to influence the conductivity of the stream (the dashed line in Figure 5.8). There was no conclusive evidence to suggest that catchment conditioning had an influence and this was not included as a separate component and is incorporated in the stemflow and throughfall signature (Figure 5.8).

5.4 Wet Antecedent Conditions (WAC)

During the autumn and winter period the passage of repeated Atlantic fronts leads to progressive saturation of the catchment (Figure 4.4). Once the catchment reaches saturation the low hydraulic conductivity of the peat implies that it remains so for a considerable period; taking a long time to drain down following an event. Consequently, during winter the most acidic upper horizons are active source areas and play an important role in generating the stream hydrological and hydrochemical response, depressing stream pH with the passage of each storm. However, the recovery time between events is often insufficient, causing a cumulative decline in pH (Figure 4.4). The pH decline stabilises at a 'steady-state' of approximately pH 3.5 to 4.0 that equates to the pH of upper peat soil water and stemflow (Wake, 1994). Once this 'steady-state' has been achieved an input of rainfall will have little effect on the catchment response, although if the event is extreme a recovery may occur.

The relationship between rainfall and the catchment hydrochemical response depends greatly on the antecedent wetness. For example, if two events rapidly follow each other the limited recovery time implies the pH response during the second event will be relatively small, irrespective of the event size (except when recovery occurs). In contrast, if the time between events is longer and allows for some recovery then even a relatively modest hydrological event can produce a large pH response.

This section examines examples of the Wet Antecedent Condition (WAC) response with respect to the event classification (Table 5.2).

5.4.1 Event 6 05 November 1996 WAC / marine / normal

Previous rainfall events had elevated the flow and the catchment was still recovering from one such event when this one began. This is reflected in elevated antecedent wetness indicators with an API = 79.8mm and pre-event flow of 75 ls^{-1}. These are much higher than the antecedent wetness indicators observed for DAC events.

The previous weather and pollution climatology was dominated by rainfall from the westerly sector. The rainfall sample chemistry, taken on 04 November, had a marine signature. The cloud mist sample analysis was incomplete but from the available determinands this also had a marine signature implying the catchment was conditioned by a marine signature. The stream chemistry, sampled on 04 November, displayed a high-flow signature with a pH of 4.5, conductivity of 76 μScm^{-1}, elevated aluminium and depleted base cation concentrations. This implies the streamflow would be a function of both the soil and deep-water components, however, the soil water signal was dominating.

Table 5.8 Event 6 05 November 1996

Hydrological Response	**Event 6 05 November 1996**
Antecedent Conditions	
API (mm)	79.9
Pre Event Flow (ls^{-1})	74.67 (05/11 at 1700)
Pre Event pH	4.50
Pre Event Conductivity	76
Prior wind direction	Westerly
Event Conditions	
Rainfall Total (mm)	37.8
Maximum intensity (mm hr^{-1})	7.8 (05/11 at 2000) 4.6 (06/11 at 1400)
Total Volume Input (Ml)	56.7
Maximum Flow (ls^{-1})	844 (06/11 at 0200) 353 (06/11 at 1900)
Number of peaks	2
Total Flow Output (Ml)	42.1
Runoff ratio (%)	74
Storm flow (%)	54
Base-flow (%)	21
Event wind direction	Westerly
Continuous Hydrochemical Response	
pH_c pulse	Yes (0.34)
pH_c Max/Min	4.64/3.80
pH_c fall during event	0.84
Does pH_c lag/coincide/lead	Lag (4 hours)
Conductivity Fall Pulse	Yes (21)
Conductivity Max/Min	117/67
C_c rise/fall during event	Rise
Does C_c lag/coincide/lead	Lag as per pH

Solutes			
Calcium (μEql^{-1})	↓	↑	↑
Magnesium (μEql^{-1})	■	↓	■
Potassium (μEql^{-1})	↓	↓	↓
Sodium (μEql^{-1})	↑	↑	↑
Chloride (μEql^{-1})	■	■	■
Sulphate (μEql^{-1})	↑	↑	↑
Aluminium ($\mu Moll^{-1}$)	↓	■	■
Iron ($\mu Moll^{-1}$)	■	■	■
DOC (mgl^{-1})	↑	↑	↑
Colour (mgl^{-1})	↑	↑	↑

Key to solutes

Concentration on rising limb	Concentration at peak flow	Concentration on falling limb

↑ Concentrations increasing.
↓ Concentrations decreasing.
■ No pattern. ND No data.

The event was in response to frontal rainfall and the catchment response can be seen in Table 5.8, Figure 5.9 and Appendix F. The frontal rainfall produced a total of 37.8 mm and is of a similar magnitude to some of the events observed in the DAC section. The catchment did not respond immediately to the rainfall, and it was approximately three hours and 4.8mm (making up the catchment deficits) before the flow increased. Interestingly, this was longer than some DAC events; this may suggest the drying and cracking of the soils during dry weather facilitates a more speedy response. The rain fell in two distinct episodes that resulted in a hydrograph with two peaks. The first peak was the largest with a flow of 844 ls^{-1}, five hours after the maximum intensity and a second peak occurred of 353 ls^{-1}.

Hydrograph separation (Table 5.8) indicates that 54% of the incident rainfall makes up the storm flow component and during the event a total of 74% of the incident rainfall was discharged at the catchment outfall. Consequently, most of the water entering the catchment was discharged during the event and only about a quarter was retained. This is clearly very different from the DAC event, however, closer examination is required before it can be decided whether the response was caused by event or pre-event water.

During Event 6 the initial pH_c was low, reflecting the antecedent wetness and the dominance of the soil and peat sub-catchment water. With the onset of rainfall, there was no change in pH_c but then it increased to a maximum, just after the maximum rainfall intensity (Figure 5.9). The initial pulse raised the pH_c by 0.34 pH units. This initial positive pulse in the pH_c is one of the distinctive features of the WAC event compared to a DAC response.

The volume, timing and short-lived nature of the initial pH_c rise suggests the pulse was derived from near channel sources that had a relatively small capacity (i.e. quickly overwhelmed). The causal mechanism of the initial pulse can be hypothesised in terms of either pre-event or event water causing the response. If the initial pH_c rise was caused by pre-event water, it implies a process such as piston flow from the bank side was operating. Piston flow is unlikely to be widespread through the poorly permeable peat and drift at Coalburn (Waterfall, 1994; Baglee, 1994). However, the peaty-gley soils have a higher hydraulic conductivity, up to three orders of magnitude (Waterfall, 1994), and therefore 'once wetted up' could transmit water rapidly during a storm. The peaty-gley soils in the south east of the catchment have also been subject to slumping/cracking, which may provide preferential flowpaths and rapid transfer of well-buffered water to drainage ditches and the main stream.

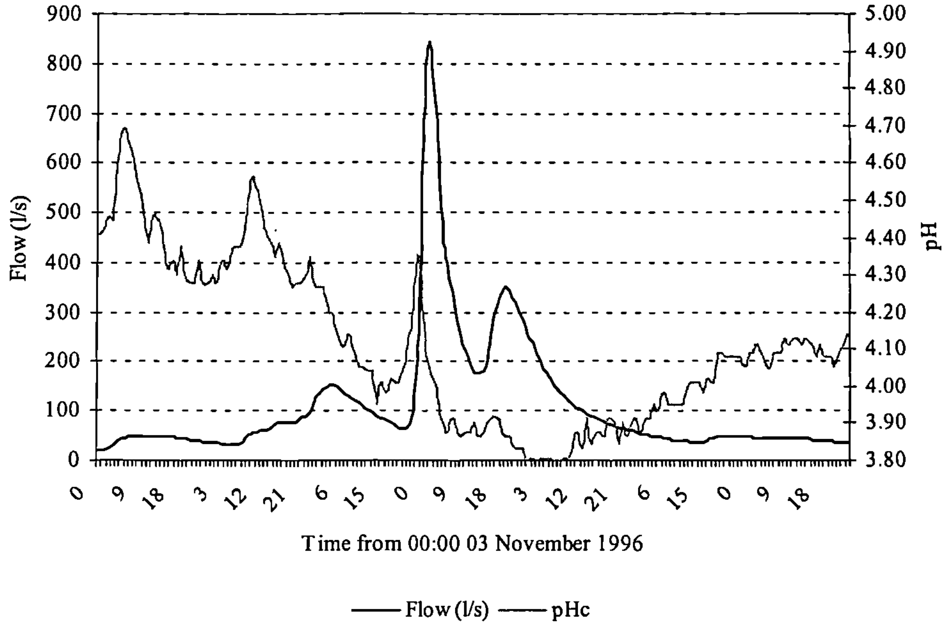
The peaty-gley sub-catchment is located close to the catchment outfall and the 'piston flow' from this area will be rapidly delivered to the catchment outfall to cause the pH_c rise.

A second pre-event water hypothesis is that between events water is stored in the drainage ditches (pers. obs.). Storage in the drainage ditches on the peaty-gley sub-catchment is well buffered compared to those draining from the peat soils (Chapter 3). Consequently, during the subsequent event the stored pre-event water will be flushed from the drainage ditches to the catchment outfall during the initial part of an event. This component will mix with contributions from the peat soils and elevate pH_c until the peat and soil water begins to dominate and the pH_c decreases.

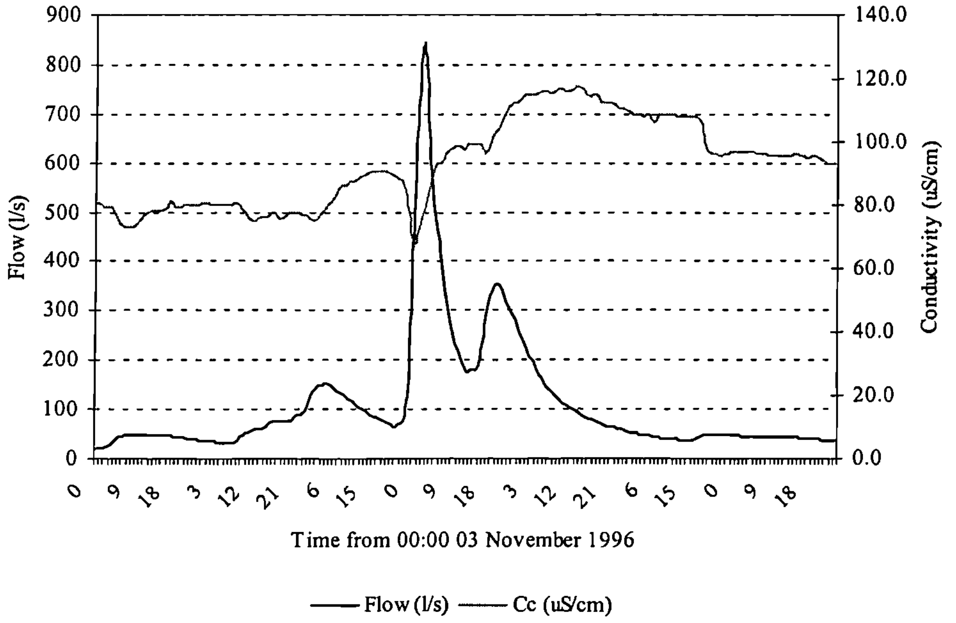
The event-water causal mechanism is based on the observation that the initial pH_c pulse, generally, occurs shortly after the maximum rainfall intensity. High intensity rain falling on a saturated catchment where the flow had already responded to the rainfall will promote lateral movement of rainfall to the forest drains and rapid delivery to the catchment outfall. Hence, the initial pulse may be a 'direct' influence of modified rainfall during the initial part of an event. The 'direct' input is likely to be greatest from the peaty-gley sub-catchment slopes are steeper and located closer to the catchment outfall. This rainfall signal will generally be of a higher pH than soil and peat sub-catchment water and will elevate pH_c slightly, until the soil and peat sub-catchment water begins to dominate again.

Figure 5.9 Coalburn Event 6 flow, pH and conductivity response

Event 6 flow and pH response



Event 6 flow and conductivity response



The magnitude of the initial pH_c pulse appears to be positively correlated with rainfall intensity (see later events). This is consistent with all the causal mechanism hypothesised; the greater the rainfall intensity the greater the volume will be delivered to the catchment outfall by the mechanism to produce the pH_c response.

The exact source and process that cause the initial rise in pH_c remain unknown; any one or a combination of the above processes may be effective and further investigation is required. The positive pH_c pulse points to the importance of the distributions of the soils in the Coalburn catchment and to the storage and chemical processes in the riparian area.

As the flow continued to increase, the soil and peat sub-catchment water began to dominate. Consequently, the initial pH_c increase was reversed and began to fall rapidly in response to the flow. The pH_c minimum lagged peak flow by four hours, implying the most acidic water did not contribute until later in the event. This is consistent with the observations made in the DAC response where the more acidic water does not contribute until this phase of the event (i.e. takes time for the soil to react and the upper more acidic horizons to contribute). Furthermore, the acidic peat sub-catchment is furthest away from the sampling site and will not contribute until later during the event.

The sample data indicated a minimum pH of 3.83, which was one of the lowest pH observed at Coalburn; equating to the pH of upper peat soil-water and stemflow (Wake, 1994). The magnitude of the pH could have a harmful effect on aquatic life at this level (Jenkins et al., 1990), however, the calcium concentrations were well above the 50 μEql^{-1} threshold throughout the event, which ameliorates the toxic effect. As the flow receded, there was no recovery of the pH_c, implying the acidic soil and peat sub-catchment water continued to contribute during this portion of the event.

During the recession limb there may be a positive relationship between pH_c and rainfall with a slight pH recovery following some bursts of rainfall. Perhaps this is caused by a similar mechanism to that described for the initial pH_c pulse.

During the second event, there was no definite initial pulse and the response was not the well defined acid event typical of Coalburn. There was only a slight decrease in pH_c for the rise in flow, again lagging the peak flow. This could reflect the saturated status of the catchment and that the preferential and most acidic pathways were already dominating; no matter how much rain entered the catchment the pH_c could not be depressed further. Relating this back to the pH-flow response (Table 4.2), this pattern of Coalburn response is Phase 3: large increases in flow can occur with little corresponding change in pH.

The flow then began to recede; however, the pH_c did not recover indicating the dominant source was still from the upper soil horizons and the peat sub-catchment. These sources continued to contribute well after the event has ceased. Consequently, the pH_c remained depressed and the event had a long recovery time. This reflects the minimal hydraulic conductivity of peat.

The initial conductivity was slightly elevated (89 μScm^{-1}), resulting from the dominance of soil and peat sub-catchment water, with the hydrogen ions making a significant contribution to the conductivity. For example, at a pH of 4.00 the hydrogen ions concentrations contribute 35 μScm^{-1} to the conductivity readings with the remainder of the conductivity being attributable to aluminium, organic and other solutes.

The conductivity response lagged the onset of rainfall and there was an initial fall in conductivity that reached a minimum just after the maximum rainfall intensity and approximately synchronous with the pH_c rise (Figure 5.9). The initial pulse resulted in a rise in pH_c of 0.35 from 4.00 to 4.35 and conductivity fell by 21 μScm^{-1}. Converting the pH_c change to hydrogen ion concentration and then to conductivity reveals that the conductivity fall of 19 μScm^{-1} could be caused by the change in pH_c alone. This implies the conductivity response was primarily driven by changes in pH_c. This may suggest that the direct influence of high pH, low conductivity rainfall in this initial phase may not occur; the dilution response can be explained by the increase in pH_c alone and any further dilution would depress the conductivity further. Consequently, this lends support to an input from the peaty-gley/deep-water that increases the pH_c and causes the reduction in conductivity.

As the flow increased, the pH_c fell, and this was mirrored by an increase in conductivity reflecting the increased hydrogen ion and aluminium concentrations. When the pH_c reached its minimum on the recession limb the conductivity reached a maximum and stabilised. During the second peak the conductivity showed a slight decrease just after maximum intensity and then increased as pH_c decreased. As with the pH_c, there was no immediate recovery as the flow receded.

The event clearly demonstrates that under wet antecedent conditions and low pH conditions the conductivity response is intrinsically related to the changes in the hydrogen ion concentrations. Indeed up to 50% of the conductivity was derived from the hydrogen ion component.

During Event 6, the evidence suggests the catchment response was controlled by the soil and peat sub-catchment water (i.e. catchment processes) with pre-event water dominating (e.g. pH_c minimum on recession limb of the hydrograph). Nevertheless, there is evidence that during periods of intense rainfall event water may reach the stream. However, this event water must have been rapidly modified by catchment processes.

Aluminium concentrations during the event fell near the initial pH_c and conductivity pulse (Appendix F), which may indicate that rainfall, peaty-gley water or deep-water were contributing, all of which are depleted in aluminium. Thereafter the aluminium concentration did not vary greatly and it is difficult to identify a distinct pattern and relate them to flow pathways. Similarly, the iron concentrations during the event are difficult to interpret, exhibiting considerable variation. In general, the iron concentrations increased during the event lagging the flow and reflecting the contributions from the most acidic sources associated with high iron concentrations (soil and peat sub-catchment water).

The DOC and colour concentration increased during the rising limb and peaked on the falling limb, close to the minimum pH_c, before falling slightly as the flow receded. The impact of the second peak was relatively minor and there was a slight increase in concentrations on the falling limb. This pattern reflects the association of DOC and colour with the soil and peat sub-catchment components, and is further evidence that the most acidic water does not contribute until the later phase of an event.

The chloride concentrations showed no definite pattern (such as an increase during the event) that could be linked to an event water influence, particularly after the maximum intensities on a saturated catchment. However, this may just be a function of the rainfall chemistry (i.e. low chloride concentrations).

From the available sulphate concentrations there was a peak on the falling limb of the first hydrograph; the concentrations then fell during the second hydrograph peak and increased during the recession limb. This was similar to the DOC/colour pattern, which suggests that the sulphate response was being driven by catchment processes.

The sodium concentrations showed an increase during the event but no relationship with the flow or rainfall; the increase might reflect the marine signature of the event water and/or the antecedent conditioning. Examining the theoretical ratios of chloride to sodium indicates that the sodium concentrations were less than expected. Whether this is retention in the catchment due to exchange in the peat (Clymo, 1984), or a function of Coalburn's inland location (i.e. 0.85 ratio not appropriate), it is not possible to say. Consequently, with the information available it is not possible to attribute the event response to a sea-salt event as per Langan (1989).

Calcium and magnesium concentrations showed the same pattern, during the first hydrograph, being diluted on the rising limb. This is consistent with an increased component of the flow being derived from the soil and peat sub-catchment water. During the remainder of the event, the concentrations increased slightly, particularly calcium. This response was not expected at this time of an event when the base cation depleted soil and peat water was dominant; however, a similar response was also observed in Event 5. It is unlikely that a greater deep-water component would occur at this phase of an event and the response must be explained by some other mechanism. The pH_c exhibited slight increases following burst of rainfall in both Event 5 and 6 and this was ascribed to initial pH_c pulse mechanism. The pH_c increase is approximately synchronous with the increase in calcium and magnesium concentrations, which could imply this was a peaty-gley sub-catchment signature. Thus, during WAC events with intensive showers on the recession limb there may be a rapid delivery of peaty-gley sub-catchment water to the catchment outfall that causes a slight recovery. The response is only transient during the rainfall (i.e. the peat sub-catchment and soil water-signal drown this signal when the rain stops).

The potassium concentrations showed a dilution response during the event and only recovered slightly on the second hydrograph recession limb. During winter foliar leaching is unlikely to be a source of potassium and the stemflow routing is likely to be less important in terms of the catchment response.

5.4.2 Event 7 21 January 1995 WAC / marine / moderate intensity

Prior to the event the flow was receding from a previous snowfall/rainfall event; this was reflected in the elevated antecedent wetness indicators, with the API = 57.4 mm and the pre-event flow of 53 ls^{-1}. The previous weather was dominated by rainfall from westerly/marine sector, this is reflected by the rainfall and cloud mist chemistry of the sample taken 02 February 1995, which had a marine signature.

The stream chemistry prior to the event was inferred from the continuous data alone. The pH_c was 4.78 and the raw conductivity 53.4 μScm^{-1}. The pH_c and conductivity exhibit a high-flow signature, which was consistent with antecedent wetness indicators.

The catchment response can be seen in Table 5.9, Figure 5.10 and Appendix G. A frontal system produced at total of 24.2 mm of rainfall (some of which were snow showers), a relatively small event compared to the previous events. The rainfall started on 21 January at 1000 and fell over 28 hours with a maximum intensity of 3.2mm hr^{-1}, a relatively low intensity event.

With the onset of rainfall, the catchment does not immediately respond and it is approximately 3 hours and 2.8mm of rainfall before the flow begins to increase after making up the catchment deficit. The hydrograph had a single peak flow of 784 ls^{-1}. Hydrograph separation (Table 5.9) indicated that 50% of the incident rainfall made up the storm flow component and during the event a total of 75% of the incident rainfall was discharged at the catchment outfall. Consequently, most of the water entering the catchment was discharged during the event and only about a quarter was retained/utilised in making up the catchment deficits.

The initial pH$_c$ was low, reflecting the dominance of soil and peat sub-catchment water (Figure 5.10). As soon as the event began the pH$_c$ began to rise and peaked at 5.02 (two hours after the maximum rainfall intensity). The initial pH$_c$ pulse was relatively small, compared to Event 6, and this reflects the lower rainfall intensity.

The flow increased rapidly and the pH$_c$ fell to a minimum of 4.34, lagging peak flow by two hours (relatively short). The causal mechanisms behind the event would not appear to be different from those discussed for Event 6. Prior to its minimum the pH$_c$ flattens off and then continued to decrease, this followed two hours of relatively intense rainfall (2.4 and 2.2 mm hr^{-1}), and this response may be caused by an input of event water. The catchment then began to recover slowly, reflecting the continued contribution from the soil and peat sub-catchment component, however, it does recover unlike the DAC events where the pH$_c$ tends to remain constant/depressed for some time after the event.

The initial conductivity was 53.4 μScm^{-1} and with the onset of the rainfall it was two hours before the conductivity responded (Figure 5.10).

Table 5.9 Event 7 21 January 1995

Hydrological Response	**Event 7 21 January 1995**
Antecedent Conditions	
API (mm)	57.4 (20/01)
Pre Event Flow (ls^{-1})	53.02 (21/01 at 1300)
Pre Event pH	4.78
Pre Event Conductivity	53.4
Prior wind direction	Westerly
Event Conditions	
Rainfall Total (mm)	24.2
Maximum intensity (mm hr^{-1})	3.2 (21/01 at 1400)
Total Volume Input (Ml)	36.3
Maximum Flow (ls^{-1})	784 (22/01 at 0000)
Number of peaks	1
Total Flow Output (Ml)	27.1
Runoff ratio (%)	75
Storm flow (%)	50
Base-flow (%)	25
Event wind direction	Westerly
Continuous Hydrochemical Response	
pH$_c$ pulse	Yes (0.19)
pH$_c$ Max/Min	5.02/4.34
pH$_c$ fall during event	0.68
Does pH$_c$ lag/coincide/lead	Lag (2 hours)
Conductivity Fall Pulse	Yes (3.1)
Conductivity Max/Min	50.3/60.3
C$_c$ rise/fall during event	Rise (10)
Does C$_c$ lag/coincide/lead	Lag as per pHc

Solutes			
Calcium (μEql^{-1})	↓	↓	↓
Magnesium (μEql^{-1})	↓	↓	↓
Potassium (μEql^{-1})	↑	↑	↓
Sodium (μEql^{-1})	↓	↓	↓
Chloride (μEql^{-1})	■	■	■
Sulphate (μEql^{-1})	ND	ND	ND
Aluminium (μMoll^{-1})	↑	↓	↑
Iron (μMoll^{-1})	↑	↓	■
DOC (mgl^{-1})	↑	↓	↑
Colour (mgl^{-1})	↑	↓	↑

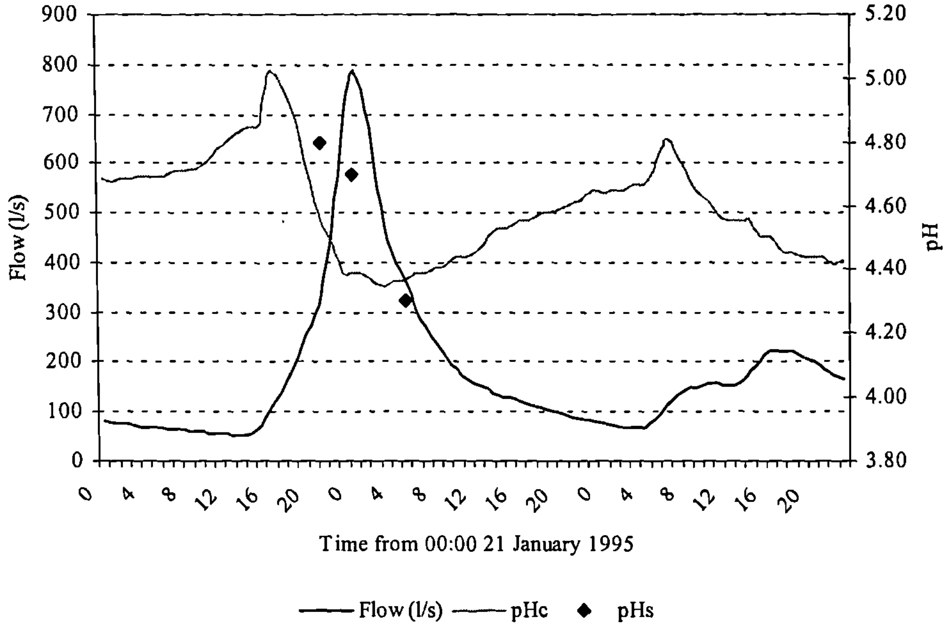
Key to solutes

Concentration on rising limb	Concentration at peak flow	Concentration on falling limb

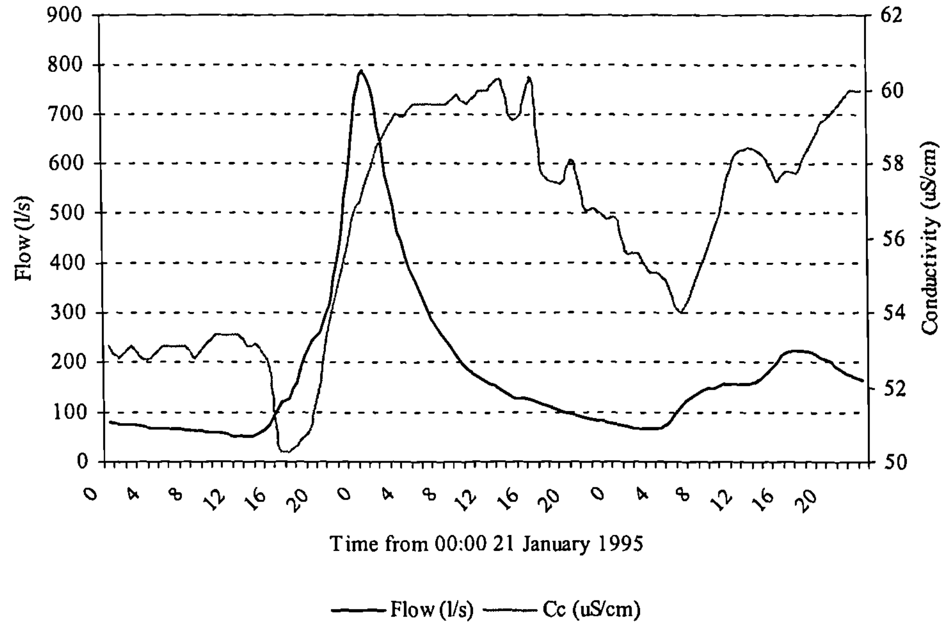
↑ Concentrations increasing.
↓ Concentrations decreasing.
■ No pattern. ND No data.

Figure 5.10 Coalburn Event 7 flow, pH and conductivity response

Event 7 flow and pH response



Event 7 flow and conductivity response



The event exhibited an initial negative conductivity pulse, falling to a minimum of 50.3 μScm^{-1}, which coincides with the maximum pH_c value. The conductivity fall was 3.1 μScm^{-1} and the theoretical fall caused by the reduction in hydrogen ion concentration is 2.5 μScm^{-1} which is close, given the measurement errors.

As the event continued the conductivity increased steeply, reflecting the fall in pH_c (i.e. the rise in the hydrogen ion concentration). The conductivity then reached a maximum of 59.3 μScm^{-1} that coincides with the minimum pH_c. The conductivity then remained roughly constant and the absolute maximum occurs at 22/01 at 1300 of 60.3 μScm^{-1}.

If the change in hydrogen ion concentration is considered in terms of conductivity during the event, it is apparent that the hydrogen ion concentration is the driving force behind changes in the conductivity. There were some periods where the change in conductivity was less than that predicted by the change in hydrogen ion concentration (generally < 5 μScm^{-1} and possibly explained by measurement errors e.g. streaming). If instrument error were the cause then this would be expected to occur throughout the event or, in the case of streaming, to be at a maximum during peak flow. However, the discrepancies tend to occur during peak flow and the recession limb. If this response were process driven then it may be indicative of a contribution of pre-event or event water that had a lower pH_c and conductivity. Thus, when comparing the expected change in conductivity, due to the increase in hydrogen ions, with the actual change in conductivity it would not be as great. Soil and peat-sub catchment water or event water (i.e. rainfall) rapidly modified in terms of pH could carry this signature.

There were only three samples taken during the event, which limits the interpretation that can be placed on them (Appendix G).

The aluminium concentrations were high on the rising limb, fell during peak flow and then increased on the recession limb. This pattern could be explained by the aluminium rich soil and peat sub-catchment water dominating during the early part of the event. However, during peak flow, the upper soil zones dominated and these are depleted in aluminium and result in a decrease in the concentrations (Chapter3, Hind, 1992; Baglee, 1994). As the flow recedes the soil water is derived from deeper in the profile and the aluminium concentration will increase as the most acidic waters (soil water and peat soil) contribute. Alternatively, this response could be explained by a component of event water, that will be depleted in aluminium, reaching the stream during peak flow (Soulsby, 1995b). DOC, colour and iron concentrations exhibited a similar pattern but the iron did not recover on the falling limb.

Calcium concentrations showed a dilution response during the event, as would be expected with the deep-water component being diluted by the soil and peat sub-catchment water. The magnesium concentrations exhibited a similar dilution response, although this was not to the same extent as calcium. The breakdown in the relationship between calcium and magnesium may be a characteristic of the WAC response. The magnesium-flow relationship indicated that magnesium concentrations could be elevated at high-flow, perhaps reflecting an input of magnesium from the marine source (Figure 3.7). Hence, the breakdown of the magnesium calcium relationship could be expected under these conditions. A plot of calcium and magnesium concentrations reveals a linear relationship especially at high concentrations (i.e. low flow) when both solutes are derived from weathering. At lower concentrations, there is more spread in the relationship perhaps, reflecting the increase in magnesium from marine sources as observed during this event.

The pattern of magnesium concentrations was similar to that for sodium, remaining approximately constant during the rising limb, peak flow and then diluted during the recession limb. This may be indicative of the rapid routing of the event water component during the rising limb and peak flow, carrying a marine influence from the rainfall. However, if this were the case, a similar pattern in chloride would have been expected (especially as chloride is conservative); however, chloride remains constant throughout the event. The theoretical values for sodium and magnesium calculated from the chloride ratio were 215 and 48 μEql^{-1} respectively, suggesting that some of the sodium may have been retained in the catchment. The magnesium concentrations could be explained by the marine input alone (it could be the deep-water component, but this unlikely as it is diluted by soil-water as demonstrated by calcium).

Potassium concentrations followed the hydrograph trace; reaching a maximum at peak flow, suggesting the stemflow and throughfall, that generally exhibit high potassium values, contribute during the event.

5.4.3 Event 8 11 November 1995 WAC / terrestrial / low intensity

On the preceding five days 15.0mm of rain had fallen and the catchment was still recovering when this event started. This is reflected in the elevated the antecedent wetness indicators; with the API = 34.1 mm and the pre-event flow 41 ls^{-1}.

The previous weather was dominated winds from the easterly sectors and some cyclonic weather; thus, there may have been some terrestrial catchment conditioning. However, the rainfall and cloud mist sample results from 14 November 1995 did not exhibit a terrestrial signature. This may be a function of the sample being taken after the marine rainfall event that would 'dilute' any previous terrestrial signature.

The antecedent river chemistry can only be interpreted from the continuous pH_c and conductivity data at the start of the event: 4.97 and 73 μScm^{-1} respectively. These are consistent with the antecedent wetness and indicate the flow a mix of soil and deepwater with the soil water dominating.

Table 5.10 Event 8 11 November 1995

Hydrological Response	**Event 8 11 November 1995**
Antecedent Conditions	
API (mm)	34.1 (10/11)
Pre Event Flow (ls^{-1})	41.27 (11/11 @ 1200)
Pre Event pH	4.97
Pre Event Conductivity	73
Prior wind direction	Easterly
Event Conditions	
Rainfall Total (mm)	15.6
Maximum intensity (mm hr^{-1})	2.4 (11/11 @ 1800)
Total Volume Input (Ml)	23.4 (11/11 @ 2300)
Maximum Flow (ls^{-1})	408
Number of peaks	1
Total Flow Output (Ml)	20.1
Runoff ratio (%)	86
Storm flow (%)	57
Base-flow (%)	29
Event wind direction	Terrestrial
Continuous Hydrochemical Response	
pH_c pulse	No
pH_c Max/Min	4.97/4.29
pH_c fall during event	0.68
Does pH_c lag/coincide/lead	Lag (5 hours)
Conductivity Fall Pulse	No
Conductivity Max/Min	73.0/85.0
C_c rise/fall during event	Rise (12)
Does C_c lag/coincide/lead	Lag as per pH

Solutes			
Calcium (μEql^{-1})	↓	↓	↑
Magnesium (μEql^{-1})	↓	↓	↑
Potassium (μEql^{-1})	ND	ND	ND
Sodium (μEql^{-1})	↑	↑	↑
Chloride (μEql^{-1})	■	■	↑
Sulphate (μEql^{-1})	↓	↓	↑
Aluminium ($\mu Moll^{-1}$)	↑	■	↓
Iron ($\mu Moll^{-1}$)	↑	↑	↑
DOC (mgl^{-1})	↑	↑	↑
Colour (mgl^{-1})	↑	↑	↑

Key to solutes

Concentration on rising limb	Concentration at peak flow	Concentration on falling limb

↑ Concentrations increasing.
↓ Concentrations decreasing.
■ No pattern. ND No data.

The catchment response can be seen in Table 5.10, Figure 5.11 and Appendix H. Frontal rainfall produced at total of 15.6 mm (23.4 Ml) and was a relatively small event compared to the previous ones considered. The rainfall started on 11 November at 1200 and fell over 18 hours with a maximum intensity of 2.4 mm hr^{-1}: a comparatively low intensity event.

The rain fell for two hours (1.8mm) before the catchment began to react; the flow then began to rise to a single peak flow of 408 ls^{-1}. The hydrograph separation (Table 5.10) shows that 57% of the incident rainfall makes up the storm flow component and during the event a total of 85% of the incident rainfall was discharged at the catchment outfall. Consequently, most of the water entering the catchment was discharged during the event and only 15% retained. This was a higher runoff ratio than observed in the previous events, despite the low intensity.

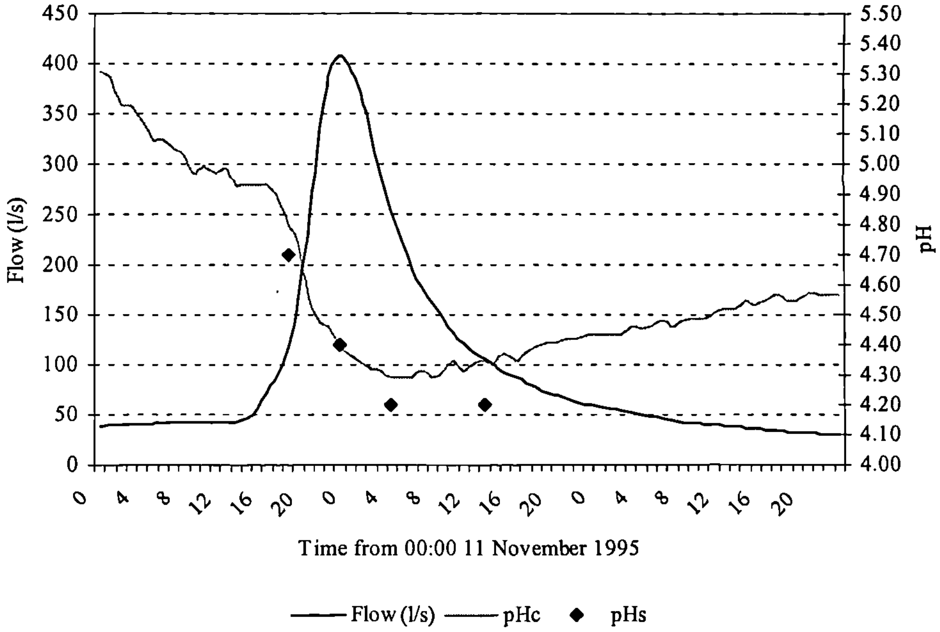
The event on the previous day had lowered the pH_c to 4.97 prior to the event, reflecting the dominance of soil-water throughflow and contributions from the peat sub-catchment (Figure 5.11). There was no distinct pH_c pulse with the onset of rainfall/maximum intensity. Perhaps this reflects the low intensity of the event, with the catchment 'wetting up' slowly and there was no direct influence from the rainfall or large enough pulse of water from the peaty-gley sub-catchment to influence the pH.

As the flow increased, the pH_c fell to a minimum of 4.29 , five hours after the peak flow. This is consistent with the hypothesis that the most acidic pathways (i.e. soil and peat sub-catchment water) do not contribute until later in the event. The low intensity nature of this event resulted in a longer lag time to minimum pH_c, which suggests that event intensity affect this characteristic of the response. The pH_c then recovered and the flow receded as the soil source water was slowly replaced by deep-water.

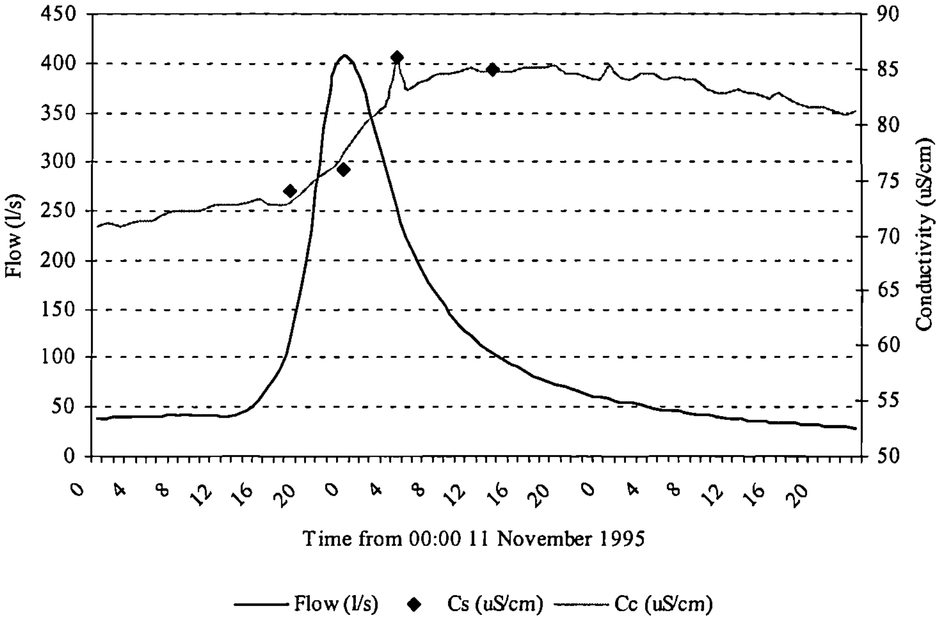
The initial conductivity was elevated due to the previous event (73.0 μScm^{-1}). With the onset of rain and following the maximum intensity, there was no definite initial conductivity pulse (Figure 5.11). However, this only serves to confirm the hypothesis that the process that controls the hydrogen ion concentration is also the primary control of the conductivity response during WAC events.

Figure 5.11 Coalburn Event 8 flow, pH and conductivity response

Event 8 flow and pH response



Event 8 flow and conductivity response



As the flow increased so did the conductivity, lagging slightly, typical of a WAC response. The conductivity had a distinct peak, which coincided with the maximum hydrogen ion concentration (i.e. minimum pH_c). The conductivity then falls slightly before recovering slowly.

Examining the change in the conductivity driven by the hydrogen ion concentration, it was apparent that during the rising limb and up to peak flow the extra contribution from hydrogen ions was not translated directly into increased conductivity. On the recession limb the conductivity and hydrogen ion change approximately agree. This phenomenon was observed in Event 7. However, while the timings are different it is likely that the same mechanisms underlie the response.

There were only four samples taken during the event, which limits the interpretation that can be placed on them (Appendix H).

The aluminium concentrations indicated a positive relationship with flow during the event, and the maximum concentration was observed at peak flow; it decreased on the recession limb. This pattern has been observed in many of the previous in events.

The iron concentrations increased throughout the event reflecting the increase component from the low pH_c soil and peat sub-catchment water. On the recession limb the iron concentration increased from 11.1 μEql^{-1} (0400) to 16.3 μEql^{-1} (1300), by which time the pH_c had begun to recover. This may reflect an input from waters derived from the peat sub-catchment.

The DOC and colour concentration exhibited a general increase during the event and reached a maximum that coincided with the lowest pH_c, as has been observed previously.

Chloride concentrations exhibited a step increase during the event, being higher on the recession limb. During the recession limb soil throughflow and the peat sub-catchment would be dominant and so the response could be due to within catchment stores rather than a direct influence from the rainfall. However, given the saturated status of the catchment, there may be an element of event water in the hydrochemical response.

Sulphate concentrations showed a definite dilution response to flow during the event. The chloride concentrations suggest that most of the sulphate observed in the stream was from non-marine sources. This may be indicative of catchment conditioning, an effect that was diluted during the event by soil and peat sub-catchment sources (and an element of event water).

Sodium concentrations indicated a slight increase during the event, perhaps reflecting the marine nature of the event. Sodium concentrations are lower than predicted from the chloride concentrations (for similar reasons discussed in previous events).

Calcium and magnesium concentrations showed a dilution response during the event, as would be expected as the deep-water component was diluted by soil, peat sub-catchment and a small element event water. There would appear to be no breakdown in the calcium-magnesium relationship that was observed for other WAC events. Thus, the breakdown in calcium-magnesium relationship may have an event threshold size and/or intensity to deliver large enough volume of event water to the catchment outfall.

5.4.4 Event 9 31 January 1995 WAC / marine / intense

The catchment was still recovering from rainfall events during the previous week, this may have included snowmelts (pers. obs.). This was reflected in the elevated antecedent wetness indicators; the API = 94.4mm and a pre-event flow of flow of 26.84 ls^{-1}. The catchment, whilst saturated, had a relatively low starting point with respect to flow.

The previous weather was dominated by rainfall (and snow), predominantly of marine origin. This was evident in the rainfall and cloud mist samples taken 02 February, which exhibited a marine signature, although the sea-salts were not elevated. This may reflect the magnitude of the storm and that a washout process occurred (i.e. the signal was diluted).

The only information available for the stream chemistry was the continuous data, the pH_c and conductivity were 4.90 and 48.4 μScm^{-1} respectively. This was consistent with the antecedent wetness indicators and the hydrochemistry would be a mix of soil and deep-water, with the soil and peat sub-catchment water dominating.

The catchment hydrological and hydrochemical response can be seen in Table 5.11, Figure 5.12 and Appendix I. The rainfall event resulted from the passage of a frontal system (and an unknown element of snowmelt), during which 73.0mm (109.5 Ml) entered the catchment in 21 hours; one of the largest events recorded at Coalburn. The rain fell in two distinct bursts:

31/01 0100 to 1200

Total Rainfall = 56.6 mm

Max intensity = 8.8 mm hr^{-1} at 0800.

31/01 1300 to 2100

Total Rainfall = 16.4 mm

Max intensity = 2.8 mm hr^{-1} at 1600.

There was a lag of approximately one hour after the rain began for the flow to respond, reflecting the saturated status of the catchment. The input signal resulted in a hydrograph with two peaks. The first peak was the highest and flows increased from 27 ls^{-1} to 2726 ls^{-1} (two orders of magnitude) in nine hours: very rapid, even for the Coalburn response. This was a product of the intense rainfall during the early part of the event (in one five hour period 37.2 mm fell (55.8 Ml)), and the improved drainage at Coalburn.

Table 5.11 Event 9 31 January 1995

Hydrological Response	**Event 9 31 January 1995**
Antecedent Conditions	
API (mm)	94.4 (31/01at 0100)
Pre Event Flow (ls^{-1})	26.84
Pre Event pH	4.90
Pre Event Conductivity	48.4
Prior wind direction	Westerly
Event Conditions	
Rainfall Total (mm)	73.0
Maximum intensity (mm hr^{-1})	8.8
Total Volume Input (Ml)	109.5
Maximum Flow (ls^{-1})	2726 783
Number of peaks	2
Total Flow Output (Ml)	89.9
Runoff ratio (%)	82
Storm flow (%)	71
Base-flow (%)	11
Event wind direction	Westerly
Continuous Hydrochemical Response	
pH_c pulse	Yes (0.66)
pH_c Max/Min	5.56/4.36
pH_c fall during event	1.20
Does pH_c lag/coincide/lead	Lead (1 hour)
Conductivity Fall Pulse	Yes (4.4)
Conductivity Max/Min	Complex, see text
C_c rise/fall during event	Complex, see text
Does C_c lag/coincide/lead	Complex, see text

Solutes			
Calcium (µEql^{-1})	ND	ND	ND
Magnesium (µEql^{-1})	ND	ND	ND
Potassium (µEql^{-1})	ND	ND	ND
Sodium (µEql^{-1})	ND	ND	ND
Chloride (µEql^{-1})	ND	ND	ND
Sulphate (µEql^{-1})	ND	ND	ND
Aluminium (µMoll^{-1})	ND	ND	ND
Iron (µMoll^{-1})	ND	ND	ND
DOC (mgl^{-1})	ND	ND	ND
Colour (mgl^{-1})	ND	ND	ND

Key to solutes

Concentration on rising limb	Concentration at peak flow	Concentration on falling limb

↑ Concentrations increasing.
↓ Concentrations decreasing.
■ No pattern. ND No data.

Maximum flow lagged the maximum intensity by one hour, again reflecting the event intensity and the saturated status if the catchment soils. As rainfall eased, the flow began to recede, at which point the second rainfall started and flow increased from 783 ls^{-1} to 888 ls^{-1} in four hours. After the rainfall ceased, the flow began to recede.

Hydrograph separation (Table 5.11) reveals that 71% of the incident rainfall made up the storm flow component, which was relatively high and reflected the event intensity and the saturated status of the catchment. During the event, a total of 82% of the incident rainfall was discharged at the catchment outfall and only 18% was retained in the catchment.

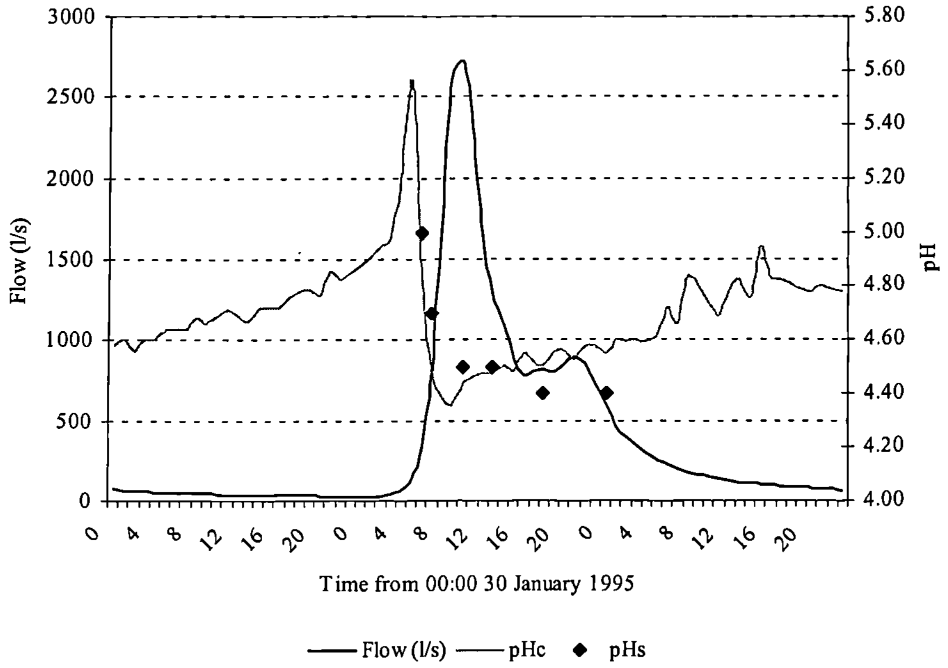
Sampled and continuous data were available for pH and conductivity, however, there was no chemical analysis for other solutes (Appendix I). Nevertheless, the extreme nature of the event means that it is important to elucidate the processes operating at Coalburn under such conditions.

The initial pH_c of 4.90 was relatively low and reflects the antecedent wetness, implying a mix of deep, peaty-gley, soil and peat water contributing to the catchment hydrochemical response. With the onset of rainfall the pH_c increased by the next reading and the event exhibited an initial pulse in pH_c, rising from 4.90 to 5.56; one of the largest recorded (Figure 5.12). The pH_c pulse occurred early during the event and the maximum rainfall intensity during this period was 3mm hr^{-1} recorded, two hours previously.

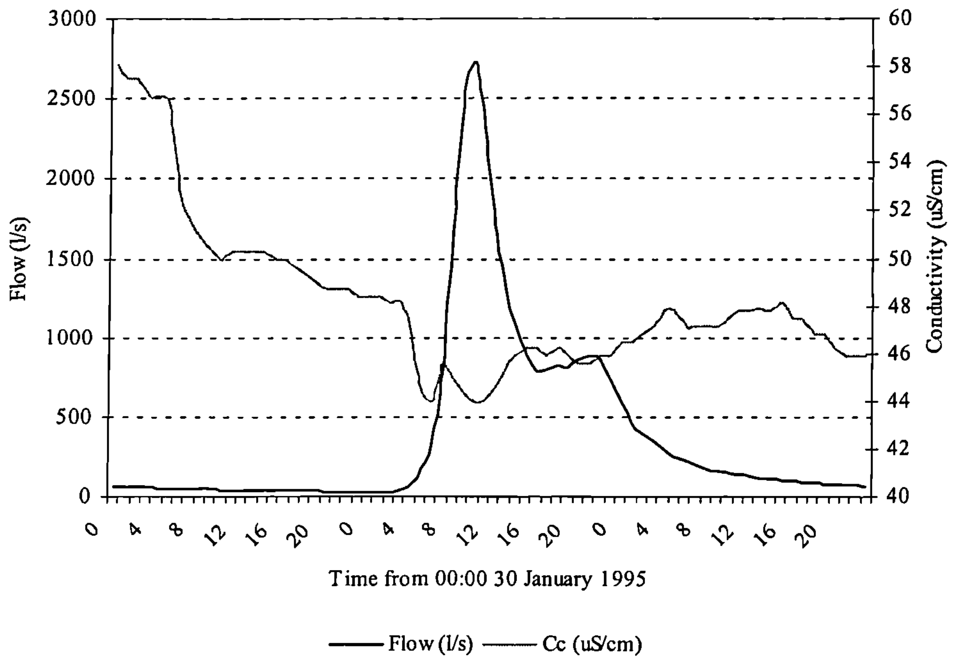
If the pH_c initial pulse was driven by a direct influence of rainfall, a concept put forward earlier, it would follow that a similar response would be expected following the maximum intensity of 8.8 mm hr^{-1} which occurred later during the event. However, no pH_c pulse was observed. The fact that the pulse still occurs at during the early phase of the event suggests it is a near stream/catchment outfall source that causes the response during wet antecedent conditions. Intense rainfall during the early part of the events serves only to amplify this signal. Consequently, piston flow or input from the peaty-gley sub-catchment are the most likely cause of the initial pulse.

Figure 5.12 Coalburn Event 9 flow, pH and conductivity response

Event 9 flow and pH response



Event 9 flow and conductivity response



As rainfall continued the flow increased and pH_c fell rapidly to a minimum, consistent with the relationship between the rapidity of the flow increase and the pH_c fall. Unusually, the event intensity resulted in the pH_c minimum occurring one hour before peak flow and lagging the maximum rainfall intensity by one hour. Following this the stream pH_c began to increase and a recovery was observed, as per Phase 4 of the pH-flow relationship (Table 4.2).

The pH_c recovery was probably a function of the catchment's saturated status and event intensity, with the more acidic soil and peat sub-catchment waters contributing earlier during the event. At this stage of the event, the catchment would have been saturated and in other similar events, large saturated areas have been observed near the stream (particularly in the peat sub-catchment). This would facilitate the rapid routing of the rainfall through a saturated canopy to the drainage ditches, streams and the outfall; allowing only a limited time for the pH of such water to be modified. Thus, it is thought the recovery was caused by a direct input of higher pH rainfall that was not fully modified by catchment processes. It then follows on that the minimum pH_c does not represent the most acidic water contributing, but the point at which the event water (i.e. rainfall) begins to influence the catchment response. This may account for the fact that the event had a minimum pH_c of 4.36, which is not very acidic compared to less extreme (volumetrically) events.

In addition there may have been a washout process operating had reduced the organic acidity during this and preceding events (Havas et al., 1984; Kullberg et al., 1993).

During the second rainfall the flow responded; however, there was no corresponding pH_c depression and the recovery continued. This probably reflects that the second event impacted on an inundated catchment where the rainfall was already having a direct influence. The second event would also exacerbate the washout of the organic acidity in the catchment, if this process were operating.

The hydrograph separation, catchment yields and pH_c response during this event suggest there is a rainfall threshold in the Coalburn response above which the input signal can overwhelm the normal flow pathways; there is rapid transfer of event water to the catchment outfall. Furthermore, during such an extreme event, with wet antecedent conditions, there could be a process operating that causes the washout of organic acidity.

The initial conductivity was 48.4 μScm^{-1} and it exhibits a complex pattern in response to the event (Figure 5.12). The conductivity had fallen over the previous few days as the catchment recovered from a previous event, driven by the rising pH_c and falling hydrogen and other ion, concentrations. With the onset of rainfall the conductivity reacted within the hour and exhibited the initial conductivity fall typical of WAC events, falling to 44 μScm^{-1} an hour after the maximum pH_c. The rise in pH_c could account for a fall of 3.4 μScm^{-1}, which suggests the pH_c change explained most of the conductivity change and the mechanism driving both the pH_c and conductivity. As flow increased, the pH_c fell and the conductivity increased slightly to a peak at the minimum pH_c. The direct influence of the rainfall then resulted in a dilution response in the conductivity that reached another minimum of 44 μScm^{-1}, coinciding with peak flow.

During the second rainfall and peak flow there was evidence of a further dilution effect from the rainfall; however, this is relatively short lived and the catchment continued to show an increase in conductivity. This contrasts with the pH_c, that showed no response and perhaps reflects the sensitivity of the conductivity under such circumstances. The rainfall can reach the stream relatively unmodified in terms of conductivity compared to the pH_c. As time progressed on the recession limb the conductivity decreased while the pH_c continued to rise.

Examining the observed change in conductivity during the event to the predicted change from the hydrogen ion concentration it is evident that dilution by low conductivity, low pH event water occurred during the event .

5.4.5 Wet Antecedent Conditions summary

The hydrochemical response for WAC events has distinct features, the first is the existence of a initial pH increase and conductivity fall for most events; following this the pH declines rapidly and the conductivity increases.

Typically, the WAC had an elevated API and pre-event flow compared to the DAC response. In terms of the Coalburn runoff model, the pre-event flow was derived from a mixture of the soil and deep-water components of the peat and peaty-gley sub-catchments (Figure 5.13). The sources of the pre-event flow was reflected in the catchment hydrochemistry with the pH

Typically, a WAC response takes the following form. With the onset of rainfall, the catchment does not respond in terms of flow or chemistry for several hours, despite being relatively saturated. This represents the storage within the canopy and the fact that some of the water will be making up the catchment deficits (Figure 5.14).

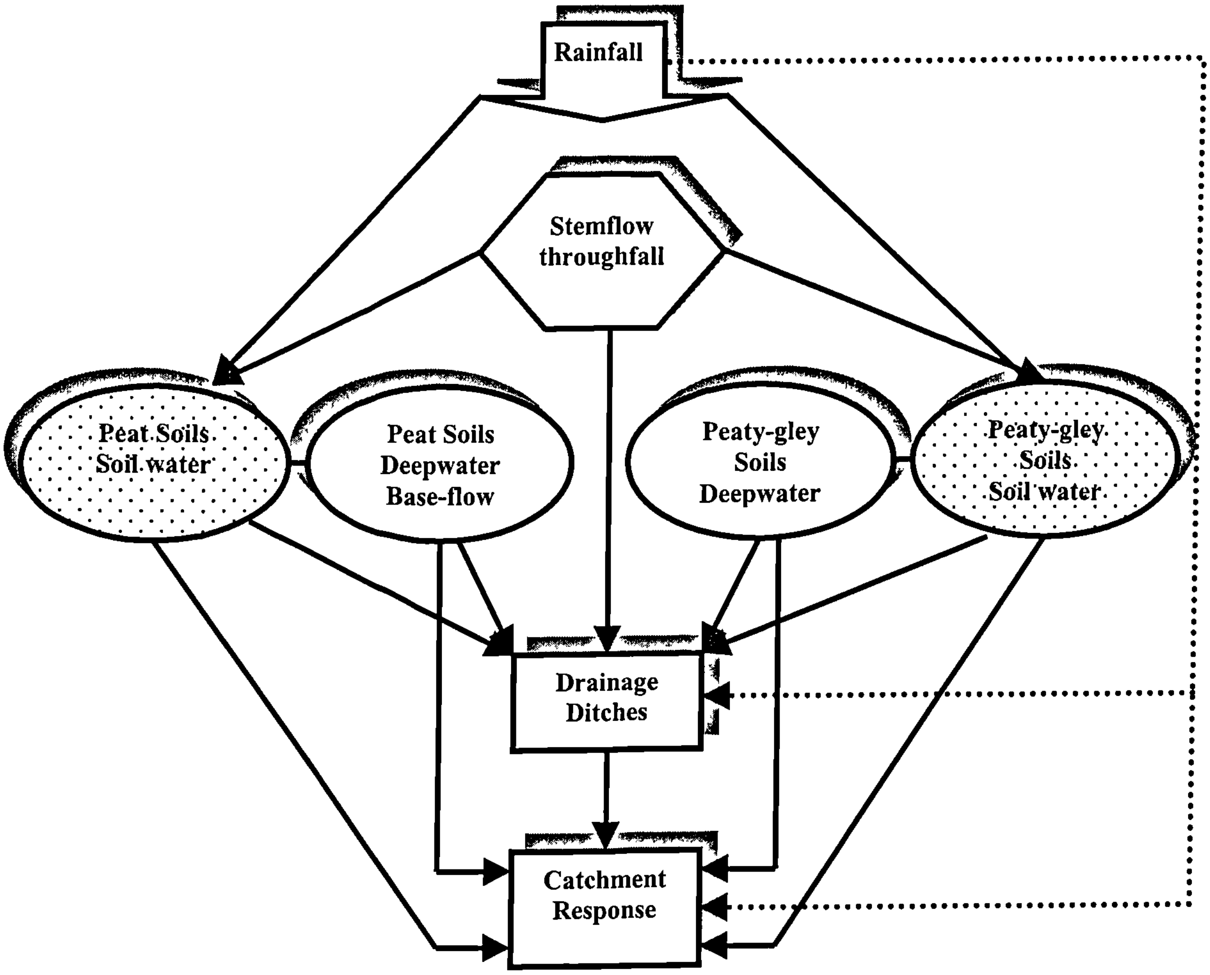
During the initial part of the event, just as the flow begins to rise, the stream chemistry exhibits an initial hydrochemical pulse, with the pH increasing and conductivity falling. The fall in conductivity has been intrinsically linked to the fall in the hydrogen ion concentration. The pH rise, volume and timing suggest the pulse must be derived from sources near to the channel and catchment outfall. The initial pulse involved small volumes, yet has a relatively large chemical impact, especially considering that the pool effect is likely to buffer changes involving small volumes of water. Observations indicate that the greater the intensity during the early part of the event, the greater the initial pulse. While the initial response is a signature of the WAC event, it does not occur for all events. An initial response was not observed for Event 8, this was a relatively small low intensity event, which suggest there is an intensity threshold required to generate the response.

The causal mechanisms put forward for the initial pulse were:

- 'Piston flow' from the bank side.
- Drainage ditch storage.
- Rainfall influence.

It is also likely that the location of the peaty-gley sub-catchment close to the catchment outfall will play a fundamental role in this response. The evidence presented here suggests that the initial pulse is most probably due to a 'piston flow' type mechanism with a source from the peaty-gley sub-catchment. However, further work is required to confirm this.

Figure 5.14 Coalburn runoff model wet antececdent conditions: event flowpaths



Key

…………… Event water component Shaded area = dominant pathway.

As flow continues to rise, there comes a point where the buffering capacity of the deep-water is overwhelmed and the pH begins to fall. The increase in flow results in a rapid decrease in pH; indeed the rapidity of the pH fall directly reflects the rapidity of the flow rise. This represents the rapid delivery of soil-water and peat sub-catchment water, that dilute/overwhelm the buffering capacity of the peaty-gley and deep-water (shaded in Figure 5.14).

The pH minimum generally lagged peak flow by several hours: its length was inversely related to the event intensity. This reflected the fact the most acidic water did not contribute until later in the event (i.e. it takes time for the soil to react and the upper more acidic horizons to contribute). Furthermore, the acidic peat sub-catchment is furthest from the catchment outfall and does not contribute until later during the event. These observations are consistent the observations made for the DAC response.

The conductivity increased with flow and reflected the increase in hydrogen ion concentration. However, aluminium, organic acids and other solutes also contribute to the increase. Hence, the mechanisms driving the pH response were responsible for the conductivity response. The conductivity mirrored the pH response, when the pH reached its minimum on the recession limb the conductivity reached a maximum, after which both slowly returned to the pre-event levels.

If the change in hydrogen ion concentration was considered in terms of conductivity during the event it was apparent that the hydrogen ion concentration was the driving force behind changes in the conductivity. There were some periods where the change conductivity was less than that predicted by the change in hydrogen ion concentration, although these were relatively small (generally $< 5\ \mu Scm^{-1}$) and could be accounted for by measurement errors. This phenomenon may be indicative of event water that is preferentially routed through the catchment and while the pH is rapidly modified by catchment processes, it still retains its low conductivity signal. This would imply a proportion of event water made up the catchment response during WAC events.

If the rainfall signal causes more than one hydrograph peak, the hydrochemical response on the secondary peaks was limited and there was no initial pulse in the pH or conductivity. This could reflect the saturated status of the catchment and that the most acidic water sources were dominating, routed along preferential pathways and limiting the hydrochemical response, other than causing a recovery. Furthermore, a ‘washout’ process may be operating.

There is a very slow recovery in the pH and conductivity following an event. The minimal hydraulic conductivity of peat implies the acidic water sources continued to contribute to the streamflow well after the event has ceased.

There was no conclusive evidence to suggest that catchment conditioning had an influence and this was not included as a separate component and is incorporated in the stemflow and throughfall signature (Figure 5.14).

By virtue of the wet antecedent conditions, the catchment can become saturated and some of the above 'classic' relationships break down. Under saturated conditions a component of the rainfall was observed to be rapidly routed to the catchment outfall (the dashed line in Figure 5.14) to cause a recovery in conductivity and some solutes. A component of the rainfall/event water signal would also pass through the stemflow and throughfall route, although this signal would be chemically modified by the catchment processes. The rapid routing of water through the upper soil horizons may also cause a 'washout' of organic acidity.

During extreme events (Event 9 - 31 January 1995), the rainfall/event water began to dominate the catchment response with the following effect on the catchment response:

- the pH responds before discharge;
- the stream then begins to recover during peak flow;
- the conductivity response becomes more complex.

This response suggests there is a threshold in the Coalburn response where the input volumes overwhelm the normal flow pathways and there is rapid transfer of event water to the catchment outfall.

5.5 Summary

Coalburn stream water quality demonstrates considerable variation according to the catchment conditions, event conditions and inferred flow sources/pathways for runoff. In terms of the research programmes objectives, the discussions during this chapter has elucidated the following:

Classification of the Coalburn hydrochemical events according to their catchment scale response, characteristics and signatures.

The concept of classifying the Coalburn events according to the antecedent and event conditions was put forward earlier in this Chapter; having examined several events it is worth considering whether events have been observed in each category (Table 5.12).

The examination of the events has highlighted that the antecedent wetness and event conditions are important in determining the catchment response. The original classification system included the antecedent pollution climatology to reflect the potential importance of catchment conditioning. However, the data gathered is not of sufficient resolution (particularly the rainfall sampling) to fully assess the differences between events with terrestrial and marine signatures, and further work is required.

Table 5.12 Coalburn acid event classification

	Event Conditions		
Antecedent Conditions	Normal	Intense	Snow or Snow Melt
Wet	✓	✓	✓
Dry	✓	✓	✖

<u>Key</u> ✓ = Event observed at Coalburn.

✖ = Event not observed at Coalburn during this study.

As with all classification systems, it can never capture the infinite variability of the catchment response, however, at a generic level the system appears to work well.

Apply hydrological principles and chemical signatures to conceptualise the likely causal mechanisms underlying the acid events at Coalburn (considering the pollution climatology, flowpaths, residence times, antecedent conditions, pre-vent and event water).

Overall, the hydrochemical response and episodic nature of the acidification reflects the catchment structure and chemical gradients (i.e. a substrate of high buffering capacity and organic rich peat surface horizons). During hydrological events, the rapid increase in flow is accompanied by an acid event, as the acidic soil-water and peat sub-catchment components become dominant. However, during intense rainfall on a saturated catchment, event water may influence the hydrochemical response.

The continuous pH and conductivity data have provided valuable information to diagnose the hydrochemical processes operating by visual appraisal alone. The episodic nature of the acidification at Coalburn has been clearly linked to: antecedent conditions; event conditions; dominant flowpath(s); mixing of event and pre-event water and the relative contributions of the deep/soil and peat/peaty gley sub-catchments.

Antecedent wetness controls the starting point of an event, i.e. whether a DAC or WAC response is observed. The event conditions (especially the distribution/timing of precipitation) are fundamental in shaping the exact nature of the response, controlling the flowpaths and residence times. For example, the higher the rainfall intensity the more rapidly flow increases and pH falls and the lag between peak flow and minimum pH is reduced.

The Coalburn hydrochemical response, particularly pH, can largely be explained by the chemical gradients and signatures within the catchment. This implies that pre-event water underlies the catchment hydrochemical response that can be explained in terms of sources, flowpaths, residence times and mixes of 'within catchment' water sources. The fact that pre-event water/catchment processes dominates implies the primary source of acidity must be the organic acids within the catchment, derived from the peat, upper solum and pine needle litter layer.

However, during ‘extreme’ events, there was evidence that event water influenced the catchment hydrochemical response, with the stemflow signature being observed in the stream and a pH and conductivity recovery occurring.

These characteristics were consistent with the previous observation that the deposition chemistry (acid oxides or sea salt events) can influence the stream chemistry during extreme events (the importance of antecedent conditioning on subsequent event chemistry was highlighted in Chapter 4). However, to confirm the exact influence of catchment conditioning on the acidity of the subsequent event would require further work including more extensive sampling and instrumentation. The influence of event water may reflect the effectiveness of the artificial drainage network, and as this becomes less effective with age the proportions of event and pre-event water may change. Indeed, in older forests it has been shown (using isotope tracing) that pre-event water dominates (Neal and Rosier, 1990).

While the chemical gradients and signatures are important it should be remembered that improved artificial drainage has a role in preferentially routing the chemical signatures to the catchment outfall; by-passing the neutralising deep-water pathways and reducing the residence time for buffering. Robinson et al. (1994) reported the improved drainage was still hydrological significant (after 22 years), and it still exercises considerable effect upon the catchment hydrochemical response after 27 years. This was highlighted by the pH and conductivity pulse observed prior to some events at Coalburn and the event water contribution, which have been linked to improved drainage.

In summary, the catchment response at the canopy closure stage of growth is a complex integration of: antecedent conditioning; catchment inputs; canopy soil and drainage effects; and event and pre-event water. The balance between these factors is critical to the hydrochemical response and changes in these will be the focus of future studies.

To produce a conceptual runoff model for the Coalburn hydrochemical response.

The Coalburn runoff model (Figures 5.1; 5.7; 5.8; 5.13; 5.14) has been a useful tool for conceptualising the mechanisms for underlying the Coalburn hydrochemical response given that each element of the model has a chemical and hydrological signature. There were no instances where an additional component was required, however, this will be examined in more detail in the next chapter during modelling of the data.

6 Coalburn: Modelling the hydrochemical response.

Overview

Coalburn hydrochemistry has distinct chemical signatures and exhibits acid episodes; the causal mechanisms have been postulated in terms of fundamental hydrological and hydrochemical principles to produce the conceptual Coalburn runoff model. However, this has been an abstract process and to introduce a robust analysis into the process, formal 'modelling' techniques are applied to the Coalburn data.

A review of the hydrochemical models revealed two groups of models; those used for short-term modelling and those used for long-term trend analysis (Neal et al., 1997b). Short-term models include mixing models, the Birkenes Model and TOPMODEL, which model the catchment response in terms of the water sources, flowpaths and residence times. In the case of Coalburn, data are available to apply mixing modelling and the Birkenes model has already been used as the conceptual basis for the runoff model. The application of TOPMODEL to the Coalburn catchment is not possible as it requires a terrain model, which was not available. Trend analysis and 'what-if' models such as Modelling Acidification in Groundwater (MAGIC) would be useful as a policy tool to predict the effect of changes in catchment/environment management at Coalburn. However, this is not the primary aim of the study and the data available cannot populate a MAGIC model.

This Chapter applies the mixing model method and principles of the Birkenes Model to illuminate the following topics:

- *Assess whether mixing modelling can be successfully applied to the Coalburn catchment and, if possible, the accuracy of the results.*
- *What does the mixing models elucidate in terms of hydrochemical processes i.e. can the Coalburn hydrochemistry be linked to varying volumes from the soil and deep-water flowpaths and contributions from the peat and peaty-gley sub-catchments.*
- *A conceptual mixing model can be produced. This combined with the runoff model can then be used to construct a Coalburn model to represent the overall hydrochemical response and processes operating at Coalburn.*

6.1 Mixing models and hydrograph separation

6.1.1 Introduction

Coalburn hydrochemical patterns have been linked to varying volumes of water from the soil and deep-water flowpaths and the different soil types in the catchment to give the Coalburn runoff model (Figure 5.1). Volumetric hydrograph separation allocated the hydrograph response to storm and base flow. However, this cannot be directly linked to the hydrochemical response i.e. the base and storm flow components do not represent the deep and soil-water signatures. For example, during wet antecedent conditions soil and peat sub-catchment water make a significant contribution at the beginning of an event; however, in terms of conventional hydrograph separation this was ascribed to base-flow. Another drawback with volumetric hydrograph separation is that it is dependent on the methodology applied; therefore any linkage to hydrological/physical processes must be tempered with caution (Beven, 1991).

Mixing models can be applied to separate the hydrochemical response into a mixture of any number of endmembers, and interpret the processes and dynamics of the chemistry/stream water supply. Endmember mixing techniques were developed for estuarine modelling (Liss, 1976) and were first applied to the freshwater environment by Pinder & Jones (1969). More recently, Neal et al. (1992), Robson (1993) and others have applied endmember mixing to the Plynlimon catchment studies using ANC. The mixing model methodology used by Robson (1993) for the Plynlimon catchments is used as the foundations for the analysis of the Coalburn data.

For mixing model techniques to be appropriate Robson (1993) highlighted that the following requirements must be satisfied:

(a) there must be two or more well defined mixing components (end-members) with distinctive chemical composition each of approximately uniform composition;

(b) there must be one or more chemical tracers which mix conservatively;

(c) the end members must be of fixed composition, with respect to these chemical tracers;

(d) there must be no other sources or sinks for the chemical tracers; and

(e) in-stream processes must not be a major chemical control for the tracer.

The main difficulty in applying mixing models to the freshwater situation is that most chemical components that exhibit a relationship with flow are chemically reactive and the constraints of a conservative mixing model implies they cannot be used. Also to make use of mixing models for chemical separation of the hydrograph on a short-term timescale it is necessary to have continuous chemical data, which is limited to conductivity and pH at Coalburn. Referring back to requirements, it is clear that conductivity does not fulfil these criteria since it is both non-conservative and exhibits temporal variations (according to the influx of rainfall and flow variations - Chapter 3/4).

Similarly, pH does not fulfil the chemical tracer requirements due to its-non conservative behaviour. However, pH is closely linked with the Acid Neutralising Capacity (ANC) that is conservative, and while ANC is not continuously monitored, it can be estimated from the continuous pH using modelling techniques (Neal et al., 1992; Robson, 1993).

For Coalburn, the only suitable continuous determinand is ANC and this limits the mixing model to two components. With endmember concentrations of ANC_1 and ANC_2, and for measured stream value ANC_{mix}, the mixing equation is given by:

$$\text{Proportion of first component} = \frac{(ANC_{mix} - ANC_2)}{(ANC_1 - ANC_2)} \qquad (6.01)$$

6.2 Acid neutralising capacity

The Acid Neutralising Capacity (ANC) measures the ability of a solution to neutralise acidity and is defined according to Reuss et al. (1986) and Robson (1993) as:

$$\text{ANC} = \sum \text{strong base cations} - \sum \text{strong acid anions} \qquad (6.02)$$

$$\text{ANC} = \sum \text{weak acid anions} - \sum \text{weak base cations} \qquad (6.03)$$

these approximate to:

$$\text{ANC} = [Na^+] + [K^+] + 2[Ca^{2+}] + 2[Mg^{2+}] + [NH_4^+] - [Cl^-] - 2[SO_4^{2-}] - [F^-] \qquad (6.04)$$

$$\begin{aligned}\text{ANC} = {} & [HCO_3^-] + [OH^-] - [H^+] - 3[Al^{3+}] - 2[Al(OH)_2^+] - [Al(OH)_2^+] \qquad (6.05) \\ & + [Al(OH)_4^-] - 2[AlF^{2+}] + [HOrg^-] + 2[Org^{2-}] - [AlOrg^+]\end{aligned}$$

where all the bracketed terms are expressed in $\mu Moll^{-1}$.

In terms of mixing models, the most important property of ANC is that it behaves conservatively; it remains unaffected by CO_2-degassing/$Al(OH)_3$-precipitation-solution changes, and by precipitation/solution of H-organic and Al-organic (humic) substances (Robson, 1993). The assumption that ANC is conservative implies that, during mixing, ion exchange and weathering reactions involving hydrogen and/or inorganic aluminium with other ions are not important (Neal et al., 1990).

The ANC could be determined using Equation 6.02 for spot samples that have full chemical analysis; however, calculation by this method gives rise to large errors, as each measurement involves analytical error that are compounded because the ANC represents the difference between two summations of similar size (Robson, 1993). Neal et al. (1992) and Robson (1993) have developed a procedure for calculating the ANC from Gran alkalinity (Gran, 1952) and because this method uses fewer chemical determinands it reduces the errors involved in calculating the ANC.

6.2.1 Gran alkalinity

The Gran alkalinity measures a solutions capacity to neutralise strong acids. It is found by titrating a solution with acid, to a pH of 4 or less, and is given by the intercept of a line fitted though the linear segment of the titration curve (Gran, 1952; Neal et al., 1992; Chapter 2). Gran alkalinity is largely determined by the amount of hydroxides, carbonates and bicarbonates, with a contribution from aluminium hydroxides and organics in solution (Lee and Hultberg, 1985). These materials buffer in specific pH ranges and during titration consume hydrogen ions (Table 6.1).

Table 6.1 Buffering in streamwater

Material	Buffering Equation	Approximate pH range
Hydroxide	$OH^- + H^+ \Leftrightarrow H_20$	pH>8.3
Carbonate	$CO_3 + H^+ \Leftrightarrow HCO_3$	pH>8.3
Bicarbonate	$HCO_3^- + H^+ \Leftrightarrow H_2CO_3^0$	8.3>pH>4.5
Aluminium hydroxides	$Al(OH)_x^{3-x} + xH^+ \Leftrightarrow Al^{3+}$	pH>4.00
Organics	$H_{org}^- + H^+ \Leftrightarrow H_2Org^0$	pH>3.00

(Source: Snoeyink & Jenkins, 1980)

For dilute acidified waters, such as Coalburn, it is unlikely that hydroxide or carbonate alkalinity will be important as the pH is usually less then 8.3. At pH 4, all the bicarbonate and hydroxyl ions have fallen to insignificant concentrations, and the inorganic aluminium species in solution (except those that are fluoride bound) will be reduced to the Al^{3+} form. Previous work by Robson (1993) demonstrated that where the stream waters were likely to have a high organic content (c.f. Coalburn DOC/TOC results Chapter3) the Gran alkalinity titration end point should be lowered to a pH of 3.00 to include the organic component in the determination. A detailed account of how to determine the organic alkalinity component where an end-point of pH 4.00 is used can be found in Robson (1993). End-points of pH 3.00 and 4.00 were used in this study for comparative purposes.

The Gran alkalinity can be expressed as follows:

$$\mathrm{Alk_{Gran}} = \mathrm{HCO_3^-} - \mathrm{H^+} + 4\mathrm{Al(OH)_4^-} + 3\mathrm{Al\,(OH)_3^0} + 2\mathrm{Al(OH)_2^+} + \mathrm{Al(OH)^{2+}} + \mathrm{Alk_{org}} \qquad (6.06)$$

$\mathrm{Alk_{Gran}}$ = Gran alkalinity in units of $\mu\mathrm{Eql^{-1}}$.

$\mathrm{Alk_{org}}$ = Organic alkalinity.

For the two titration end points the following terminology is adopted (Neal et al., 1996):

End Point pH = 4.0 $\mathrm{Alk_{Gran1}}$ = Bicarbonate alkalinity.

End Point pH = 3.0 $\mathrm{Alk_{Gran2}}$ = Bicarbonate and organic alkalinity.

At Coalburn, the main stream exhibits pH less than 4 in some instances, whereas the streams on the peat sub-catchment have pH less than 4 for most of the time. Where the pH was less than 4 and the calculated titrant strength have a valid result, the Gran Alkalinity was determined from the intercept. However, as the pH lowers the calculated titrant strength indicates the intercept method is not applicable. Under these circumstances the bicarbonate and aluminium related alkalinity can be assumed to be zero (Table 6.1); equation 6.06 becomes:

$$\mathrm{Alk_{Gran}} = -\mathrm{H^+} + \mathrm{Alk_{org}} \qquad (\mathrm{pH} < 3.8) \qquad (6.07)$$

The Gran intercept method was only applicable to a limited number of samples with pH between 4.00 and 3.80 (approx.). Where the pH was less than 3.8, there will be a component of the $\mathrm{Alk_{org}}$, although some of its buffering capacity will already have been utilised. Hence, in relative terms the $\mathrm{Alk_{org}}$ component would be small compared to the hydrogen ion contribution that will begin to dominate as the pH falls to pH 3.0 ($\mathrm{H^+} = 1000\ \mu\mathrm{Eql^{-1}}$). Consequently, for these few samples the $\mathrm{Alk_{org}}$ has been assumed to be zero in equation 6.07.

6.2.2 Linking ANC and Gran alkalinity

While Gran alkalinity is unaffected by CO_2 degassing, it is non conservative with respect to precipitation of $Al(OH)_3$ and organic substances and is not suited for direct use in endmember mixing, consequently it is necessary to link Gran alkalinity and ANC as follows (Robson, 1993):

$$ANC - Alk_{Gran1} = -3\{Al^{3+} + Al(OH)^{2+} + Al(OH)_2^{+} + Al(OH)_3^{0} + Al(OH)_4^{-}\} \quad (6.08)$$
$$- 2AlF^{2+} - 2AlOrg^{+} - 2AlOrg^{+} - 2Al(OH)Org^{0} + (Org^{2-} + HOrg^{-})$$

The total aluminium, Al_t ($\mu Moll^{-1}$), is known and is equal to the sum of the aluminium species in solution. Thus,

$$Al_t = Al^{3+} + Al(OH)^{2+} + Al(OH)_2^{+} + Al(OH)_3^{0} + Al(OH)_4^{-} + AlF^{2+} + AlOrg^{+} \quad (6.09)$$
$$+ Al(OH)Org^{0}$$

The total organics Org_t ($\mu Moll^{-1}$) are defined as:

$$Org_t = H_2Org^{0} + HOrg^{-} + Org^{2-} + 2Al(OH)Org^{0} + AlOrg^{+} \quad (6.10)$$

The aluminium and organic terms are now substituted in to equation 6.08, it reduces to a much simpler form:

$$ANC = Alk_{Gran1} - 3\,Al_t + Org_t - H_2Org^{0} + AlF^{2+} \quad (6.11)$$
$$\approx Alk_{Gran1} - 3\,Al_t + Org_t \quad (6.12)$$

However, at Coalburn the organic buffering component was included as the end point of the titration was pH 3.0. It is assumed that H_2Org^{0} and AlF^{2+} are small which is the case for other similar studies (Robson, 1993); consequently:

$$ANC \approx Alk_{Gran2} - 3\,Al_t \quad (6.13)$$

6.3 Estimating ANC at Coalburn: patterns and relationships

6.3.1 Alkalinity measurements

Several alkalinity measurements were made at Coalburn during this study, as follows:

1. Environment Agency (Alk_{GranEA}) End point pH = 4.5
2. Newcastle University (Alk_{Gran1}) End point pH = 4.0
3. Newcastle University (Alk_{Gran2}) End point pH = 3.0

The sample data up to 21 August 1998 for these measurements is summarised in Table 6.2. The Environment Agency data calculated Gran Alkalinity (Chapter 2) using an end point of pH 4.5, which is suitable during base-flow conditions. However, during high-flow conditions Coalburn pH was often less than 4.5 and the laboratory did not report the results. Hence, for the Environment Agency data the ANC could only be calculated for the base-flow samples and there was often no data for the high-flow events (of the most interest). For the Environment Agency data there was no relationship between DOC and alkalinity (Figure 6.1), which suggests the contribution of the Alk_{org} in the range of observed samples was relatively minor, which may be expected as the bicarbonate alkalinity would be dominant.

The Newcastle University data calculated Gran alkalinity according to the Institute of Hydrology method (Chapter 2). In this instance, a number of end-point values were used (pH 4.5, 4.2, 4.0 and 3.0) to allow the study to assess the effects of the different methodologies on the Gran alkalinity result.

A comparison of Gran alkalinity derived from the different end-points can only be carried out where sample pH > 4.5 (i.e. a result is available for all the methods). The theoretical considerations imply the Newcastle University Alk_{Gran2} measurements were the most accurate as the Alk_{org} component was included, and the other methods are assessed in comparison to these results.

Table 6.2 Alkalinity at Coalburn

a) Environment Agency Data

	River	SM8	SM2	SM13	SM D/S 5	SM5	SM7	SM12	SM10
Mean	244(15)*	-14	199	588	394	617	388	572	369
Max	1616	ND	364	1148	1278	1348	1142	1412	972
Min	-56	ND	106	262	-16	186	6	100	-18
N	56	1	5	3	5	8	4	4	5

Note limitations of method in text.

b) Newcastle University Alk$_{Gran2}$ Data

	River	SM8	SM2	SM13	SM D/S 5	SM5	SM7	SM12	SM10
Mean	196	-328	271	326	262	493	165	150	314
Max	1274	459	793	1284	1300	1322	1178	1184	1124
Min	-398	-794	8	-190	-73	27	-167	-158	-109
N	26	27	24	25	26	22	26	25	26

Key to tables All values are arithmetic means except (15)* which is flow weighted.

Units All units are in μEql^{-1}

ND – no data

The variation between the results from the different end-points (Table 6.3) demonstrates that the Alk$_{GranEA}$ and Alk$_{Gran1}$ underestimate the true alkalinity (Alk$_{Gran2}$) this is the consistent with the theoretical considerations as these results do not include the Alk$_{org}$ component. The bias is greatest for the Alk$_{GranEA}$ that has the highest end point (pH = 4.5).

The percentage difference between the methods is related to the original sample pH, with the difference increasing as the pH falls. At high pH the samples have elevated alkalinity values dominated by the bicarbonate component and all the three methods produce similar results. In contrast, at lower pH the soil and peat sub-catchment water dominates and the aluminium and organic and alkalinity component increases in importance, consequently the differences between the methods and results increase.

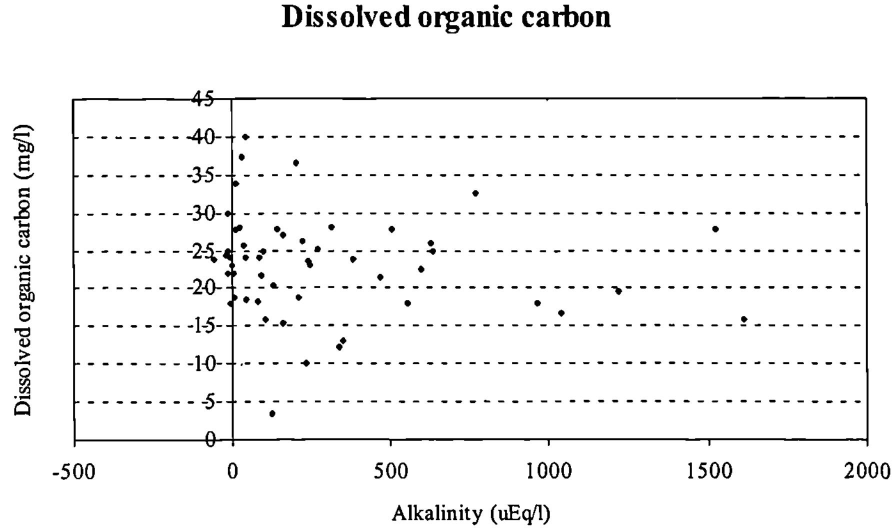
Table 6.3 Summary of percentage difference between alkalinity methods

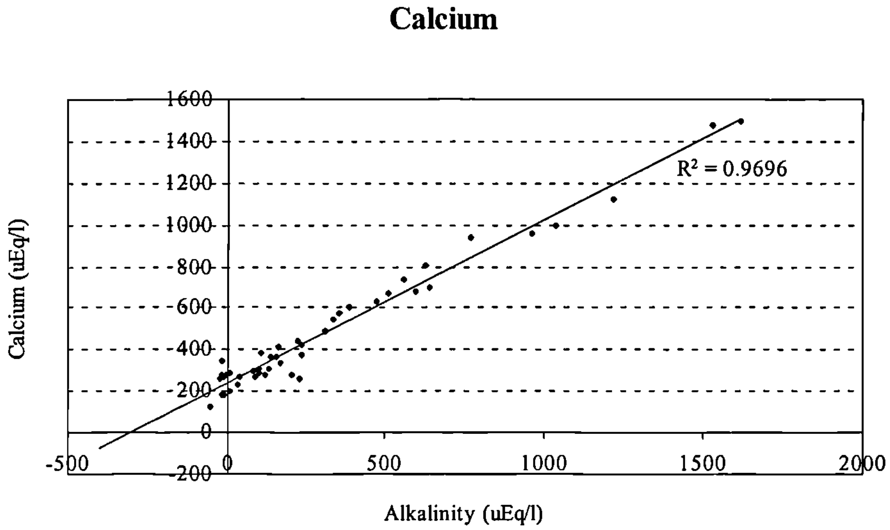
	$\mathrm{Alk}_{\mathrm{GranEA}}$	$\mathrm{Alk}_{\mathrm{Gran1}}$
Mean	-4.1	-3.0
Standard Deviation	18.3	26.9
Maximum	44.0	49.8
Minimum	-41.0	-65.4

Analysis of the different methods imply it would be inappropriate to apply a blanket correction to the $\mathrm{Alk}_{\mathrm{GranEA}}$ and $\mathrm{Alk}_{\mathrm{Gran1}}$ to take into account the organic component; this would have to be calculated using the method derived in Robson (1993). Furthermore, it is not possible to de-couple the analytical error from that caused by the organic component. For example at low pH, the alkalinity results are sensitive to the volume of titrant added and only a small change in the volume can have a significant effect on the results. With a higher original pH this factor becomes less important.

In summary, the $\mathrm{Alk}_{\mathrm{Gran2}}$ has been used as the primary data for the subsequent analysis, however, only a limited number of samples are available. A greater number of $\mathrm{Alk}_{\mathrm{GranEA}}$ sample results were available and these results are included with the health warning that the low alkalinity results do not include the $\mathrm{Alk}_{\mathrm{org}}$ component; at high alkalinity the $\mathrm{Alk}_{\mathrm{org}}$ this factor is less important.

Figure 6.1 Coalburn alkalinity, calcium and dissolved organic carbon relationships





6.3.2 Calculating the ANC for Coalburn

The Acid Neutralising Capacity (ANC) can be approximated by the following equations, for $\text{Alk}_{\text{Gran2}}$ and $\text{Alk}_{\text{GranEA}}$:

$$\text{ANC} \approx \text{Alk}_{\text{GranEA}} - 3\text{Al}_t + \text{Org}_t \qquad (6.12)$$

$$\text{ANC} \approx \text{Alk}_{\text{Gran2}} - 3\text{Al}_t \qquad (6.13)$$

In the case of equation 6.13 the complex process of estimated organic alkalinity is not necessary and this is likely to increase the precision of the ANC estimate. However, the Newcastle University data does not have a corresponding aluminium concentration, and while this would have been the ideal sampling strategy the limited resources available for the research programme at Coalburn precluded this option. Aluminium concentrations were available for the catchment outfall and exhibit a distinct relationship with flow, and a model has been derived linking the two, as follows:

$$\text{Aluminium } (\mu\text{Moll}^{-1}) = (17.25.\ln(\text{flow}) + 94.362)/26.9815 \qquad (6.14)$$

R^2	0.534
Standard Deviation	37.52
Standard Error	2.74
N	187

While the degree of scatter is relatively high and there is a positive bias at high flows, this is the best data available. Where the Environment Agency and Newcastle University data coincide the Environment Agency sample value has been used, and in all other cases the aluminium concentration has been estimated using equation 6.14.

Combining both sets of data the ANC at the catchment outfall gives eighty two samples with an ANC mean (arithmetic) of 229 μEql^{-1} and a range of 1612 to –413 μEql^{-1} and implies the Coalburn catchment is transitional catchment as defined by Harriman et al. (1990). The range of ANC values is large compared to other studies such as Plynlimon (Neal et al., 1992; Robson, 1993) reflecting the distinct vertical and spatial gradients in the catchment.

However, the range of values indicates that the Coalburn catchment could be sensitive to environmental management (cf. Chapter 7).

The ANC is flow dependent, reflecting the chemical gradients within the catchment; at low flow it is high and it falls with increasing flow as concentrations of hydrogen and aluminium ions increase in storm waters (Figure 6.2). The ANC relationship follows the same pattern with flow as the described for pH in Table 4.2. Given this, it is not surprising the ANC is closely linked to the pH and hydrogen ion concentration (Figure 6.3) and exhibits a distinctive pattern. In the pH range 5.00 to 6.00 the ANC gradually declines; however, above pH 6.00 the ANC increases exponentially with pH and vice-versa, for when the pH is less than 5.00.

The charge balance alkalinity (CBALK) was used as a data validation tool (Chapter 2): it approximates to the calculation of ANC by equation 6.04. The ANC_{CBALK} (i.e. the charge balance ANC) was examined and produces very similar patterns to those observed for the ANC_{Gran} (i.e. the ANC determined by the Gran Alkalinity method). This would suggest the assumption that the H_2Org^0 and AlF^{2+} component of alkalinity were small are valid.

Figure 6.2 Coalburn ANC - flow relationship

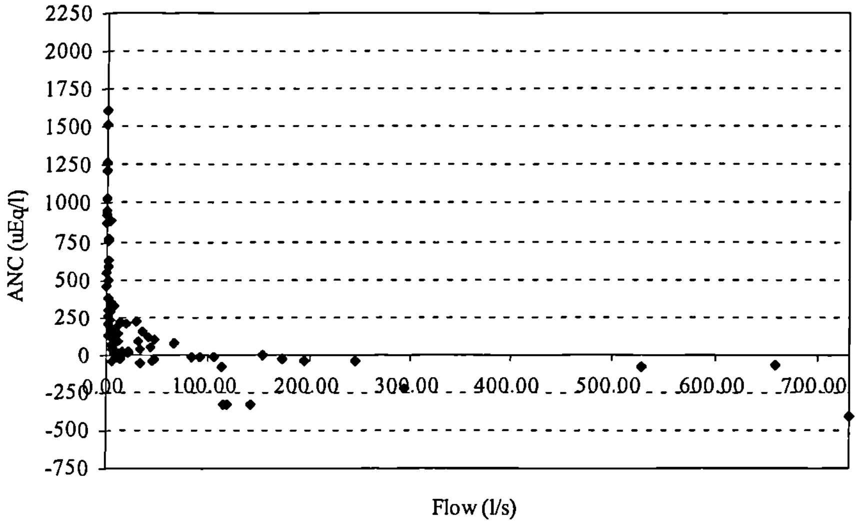
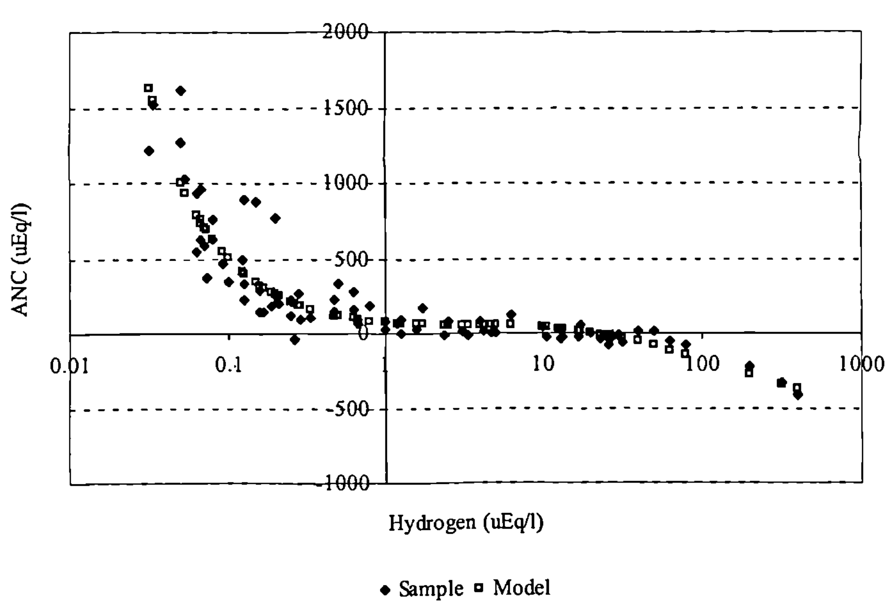


Figure 6.3 Coalburn ANC – hydrogen ion relationship



6.4 Endmember mixing model

The aim of the mixing model is to allow the separation of the Coalburn hydrochemical response into two components to account for the difference between the high and base-flow waters. To do this, an ANC value is required for each endmember.

6.4.1 The base-flow endmember

The first distinct chemical signature is the base-flow endmember, and this was estimated by analysing the Coalburn base-flow composition at the catchment outfall, as no groundwater samples were available with suitable measurements. In section 3.5.3 the base-flow chemistry was characterised from flows less than the 90 percentile mean daily flow of 0.68 ls^{-1}; this was used to calculate the ANC of the base-flow endmember. In this instance, both the ANC calculated from the Alk_{GranEA} and Alk_{Gran2} can be used; the bicarbonate alkalinity is likely to be the dominant component of the ANC under these conditions.

Six samples fit this criteria with ANC values ranging from 1612 to 552 μEql^{-1}. A regression equation was fitted to the ANC flow relationship to estimate the mean ANC at low flows (Figure 6.4).

Mean ANC = -2140.2 . Flow + 1910.2 (6.14)

R^2 0.8422

SE 157

N 6

The lowest sampled flow used in the derivation of equation 6.14 was 0.23 ls^{-1}; this translates to an estimated mean ANC of 1418 μEq/l^{-1}. It would be unwise to extrapolate equation 6.14 back to zero flow, i.e. try to estimate the mean ANC of the base-flow source, as the ANC has an exponential relationship with flow and changes very rapidly at low flows (Figure 6.2; Robson, 1993).

The same method was applied to the ANC_{CBALK} data and this produced the equation:

Mean ANC_{CBALK} = -1844 . Flow + 1941.6 (6.15)

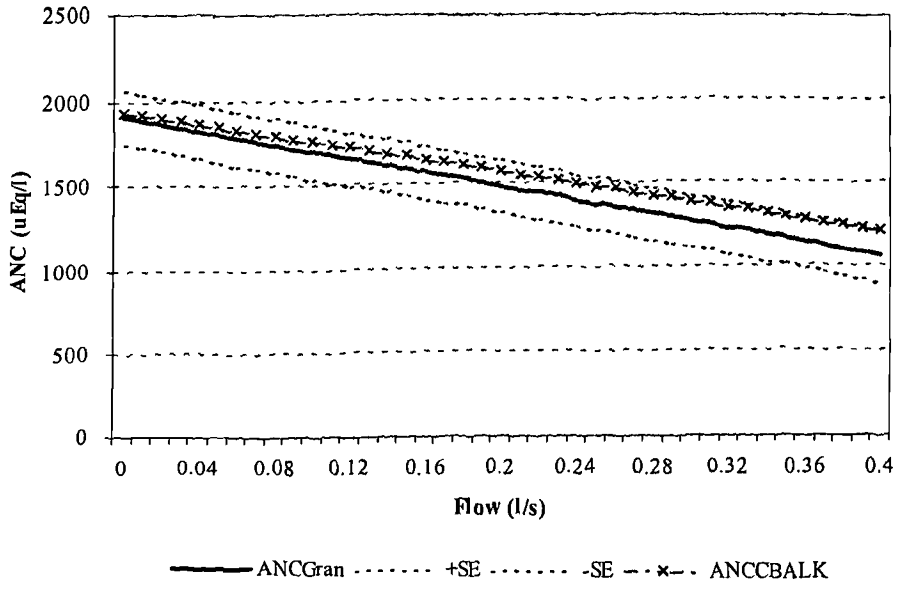
R^2 0.7638

N 6

Comparing the equations, they are similar with the ANC_{CBALK} equation within the standard error range of the ANC_{Gran} equation (Figure 6.4). More importantly, the two equations converge as the flow diminishes which suggests they both approximate to the same base-flow endmember source (Figure 6.4). This point is useful as the similarity of the equations implies the estimated mean ANC_{Gran} relationship can be extended to a flow of 0.08 ls^{-1} and the results are still valid within the standard error of the equation. This allows for a more representative estimate of the base-flow endmember to be derived. The estimated mean ANC_{Gran} calculated for a flow of 0.08 ls^{-1} is 1739 μEql^{-1} (using equation 6.14).

Thus, the base-flow endmember identified for Coalburn is 1739 μEql^{-1}, however, until a lower flow or the groundwater is sampled the true value of the endmember will remain unknown. For mixing models it is assumed the endmembers are defined, distinct and of uniform and fixed composition. The base-flow endmember has been defined; it is distinct and the values appear to be relatively constant. There is some variation in the base-flow chemistry that may be indicative of chemical gradients within the base-flow endmember and its flowpath and residence time (Robson, 1993). This introduces an uncertainty into the assumptions made for endmember mixing analysis. However, these can be considered by taking the standard error (i.e. ± 157 μEql^{-1}) of the estimated base-flow ANC when determining the proportion of base-flow (P_{base}) in the mixing model.

Figure 6.4 Derivation of low flow endmember



6.4.2 The high-flow endmember

The base-flow endmember cannot explain the hydrochemistry observed during hydrological events with the pH, ANC and other chemical parameters exhibiting concentrations outwith the base-flow chemical signature (Chapter 3). This implies a second 'high-flow' endmember is required to explain these observations.

The peat sub-catchment water has a similar composition to the high-flow signature and was selected as being representative of this endmember. Other studies have utilised soil-water samples to estimate the high-flow endmember but the variability of soil-water chemistry through time and space makes identification of this endmember problematic (Neal et al., 1992; Robson, 1993). Variability in the soil-water also contrasts with the hydrochemical response at the catchment outfall, which is regular/smooth (i.e. the soil heterogeneity and rainfall variability is integrated into a smooth response at the catchment scale). To incorporate an element of the integrating effects and reduce the uncertainty associated with estimating the soil-water endmember the low order streams and drainage ditches in the Coalburn catchment were sampled on several occasions for endmember identification purposes.

Samples of the streams and drainage ditches on the peat area were taken at SM7, SM8, SM10 and SM12. Examining the pH and alkalinity data from these sites it was apparent the data from SM8 was more consistent with the high-flow signature observed at the catchment outfall and this was used to estimate the high-flow endmember (Table 6.2). The acidity of SM8 was particularly discernible during base-flow periods when the pH at sites SM 7, 10 and 12 were greater than 6 while site SM8 remained low (pH < 5). Cryer (1978) (in Robson, 1993) sampled peat waters in the pH range 6.00 – 7.00 for a catchment near Plynlimon and Robson (1993) observed well-buffered waters at depth in the peat of the Afon Gwy catchment. These observations were ascribed to a process of upward filtration of waters from beneath the peat that elevated the pH of waters from these sites. A similar mechanism could be effecting sites SM 7, 10 and 12 during base-flow periods, but would require further investigation to confirm.

For site SM8 the ANC values were estimated from the Alk_{Gran2} and aluminium concentrations. Only samples where the flow at the catchment outfall was greater than 12.44 ls^{-1} (> 50 %ile MDF) were used to calculate the high-flow endmember and the sample on 01 July 97 was removed as an outlier. Synchronous aluminium concentrations were not available; however, several aluminium samples were taken at site SM8 during the Environment Agency's spatial sampling and these are utilised. It should be noted that in calculating the ANC the aluminium term is relatively small compared to the Alk_{Gran2} component due to the high hydrogen ion concentrations. The Alk_{Gran2} and aluminium concentrations for SM8 are summarised in Table 6.4.

Table 6.4 Summary of alkalinity and aluminium concentrations at SM8

	Alk_{Gran2}	Aluminium
Arithmetic Mean	-579	9.90
Flow Weighted Mean	-638	9.34
Maximum	-137	11.55
Minimum	-794	4.87
Standard Deviation	240	2.16
Standard Deviation Corrected	252	2.31
Standards Error	76	0.82
Number	11	8

Concentrations Alk_{Gran2} in μEql^{-1} and aluminium in $\mu Moll^{-1}$.

Standard Deviation corrected with Bessels correction as $n < 30$ (Hammond and McCullagh, 1974).

Using the flow weighted Alk_{Gran2} and aluminium, the ANC of the high-flow endmember is estimated as –666 μEql^{-1}. The mixing model assumes that the endmember is defined, distinct and of uniform and fixed composition. However, although the high-flow endmember has been defined and is distinct from the base-flow endmember, it is not of uniform and fixed composition, due to the following:

1. There are significant spatial trends within the Coalburn catchment and data from SM8 may not represent the high-flow endmember for the whole catchment;
2. There are significant temporal trends in the endmember composition with flow and season.
3. The are significant variations in the volumes and chemistries of waters from different parts of catchment during any one event.

These factors introduce errors that could affect the endmember mixing analysis. However, in any model of an infinitely dynamic natural system it is never possible to fully parameterise the variables and variability. The standard error of the Alk_{Gran2} and aluminium in Table 6.4 are utilised to approximate the error in the high-flow endmember; however, it should not be regarded as an exact measure of the uncertainty (Robson, 1993).

6.4.3 Summary of endmembers and uncertainty/sensitivity in the endmembers

The base and high-flow endmembers have been identified and are summarised in Table 6.5 and Figure 6.5. There were no spot-samples outwith the endmember range; probably reflecting the distinct nature of the endmembers at Coalburn and the large range between them especially when compared to other studies (Neal, 1992; Robson, 1993).

Table 6.5 Coalburn endmember summary

	Mean	Maximum	Minimum
High-flow Endmember	-666	-588	-745
Base-flow Endmember	1739	1896	1582

Units in μEql^{-1}

The range of endmember values represents the best estimates from the current data and sensitivity analysis will accommodate some of the errors introduced through the methodology and assumptions used.

The following uncertainty analysis takes theoretical ANC values between 1650 and –500 μEql^{-1} (the range of values observed at Coalburn) at 50 μEql^{-1} intervals and calculates the proportion of base-flow (P_{base}) using the mixing model (Equation 6.01). To assess the uncertainty in P_{base} the base-flow endmember was held constant and the high-flow endmember varied according to the range of values in Table 6.5. The process was then repeated for a constant high-flow endmember (Figures 6.5; Figure 6.6; Table 6.6).

$$\text{Proportion of base-flow} = \frac{(ANC_{stream} - ANC_{high})}{(ANC_{base} - ANC_{high})} \qquad (6.01)$$

The analysis indicated the effect of varying the endmember is greatest where that endmember is dominant, i.e. when flows are low and P_{base} is high it is most sensitive to varying the base-flow endmember; varying the high-flow endmember has little effect . In contrast, when P_{base} is a its minimum, the variation in the high-flow endmember has the most effect. In the intermediate range the P_{base} is sensitive to variations in both the high and base-flow endmember.

Table 6.6 Summary of sensitivity and uncertainty in P_{base}

	P_{base}	P_{base} HFMAX	P_{base} HFMIN	P_{base} BFMAX	P_{base} BFMIN
Mean	0.51	0.52	0.46	0.47	0.54
Maximum	0.96	0.96	0.90	0.90	1.03
Minimum	0.05	0.08	0.02	0.05	0.05
Standard Deviation	0.27	0.26	0.26	0.26	0.29
Number	45	45	45	45	45

Key Pbase = Proportion Base
HFMax/HFMin = High-flow endmember maximum and minimum value.
BFMax/BFMin = Base-flow endmember maximum and minimum value.

Robson (1993) and Beven (1991) used the following method to analyse the errors in application of mixing models that calculates the variance in P_{base} using:

$$\mathrm{Var}(P_{base}) = \frac{(ANC_{stream} - ANC_{high})^2\,\mathrm{Var}\,(ANC_{soil})}{(ANC_{base} - ANC_{high})^4} + \frac{(ANC_{stream} - ANC_{base})^2\,\mathrm{Var}(ANC_{base})}{(ANC_{base} - ANC_{high})^4}$$

This assumes the errors are independent and normally distributed and, the errors in the ANC derivation are small compared to the errors in the endmember.

Figure 6.5 Coalburn high and base flow endmembers

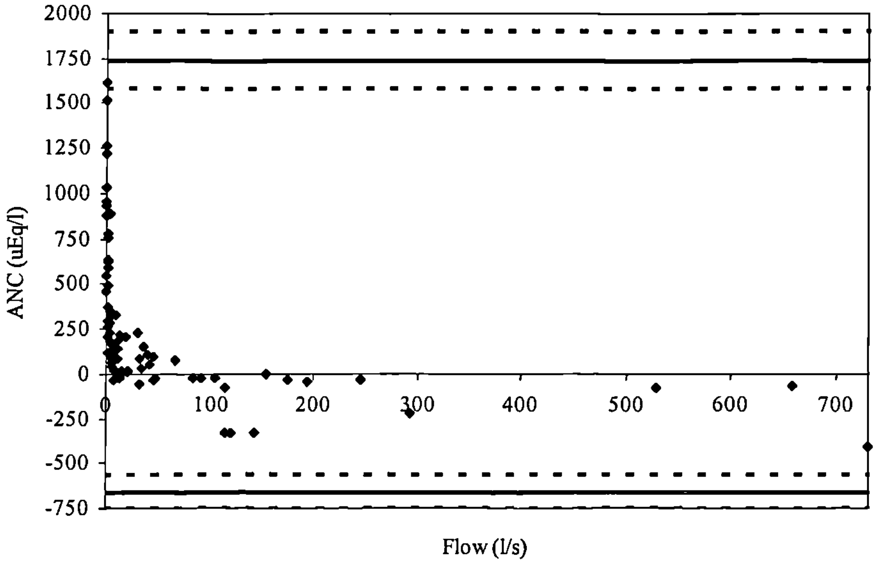
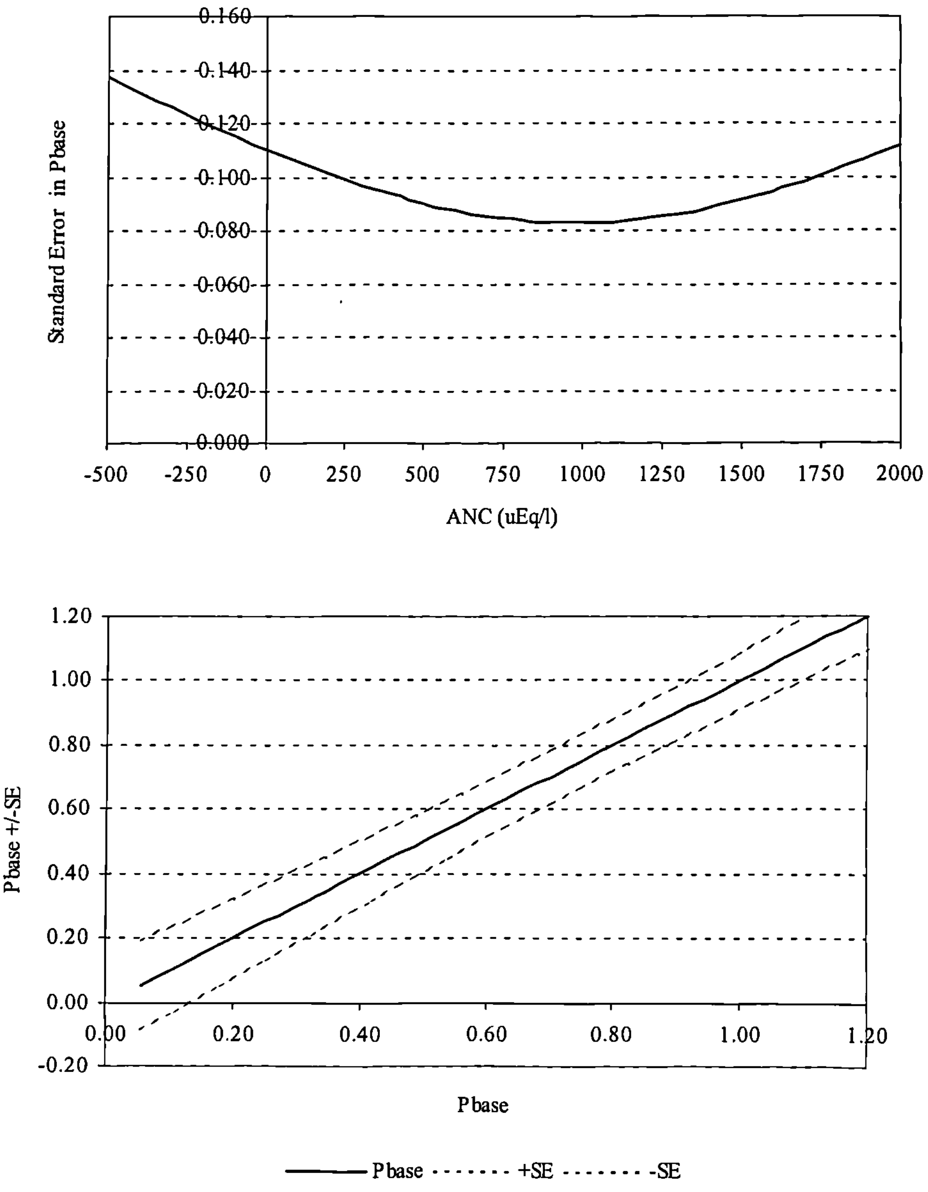


Figure 6.6 Endmember sensitivity analysis



Results from applying this method to the Coalburn data reveal the standard error in P_{base} is relatively small (maximum 0.14). The standard error in the P_{base} exhibits a parabolic shape; the minimum error is associated with ANC range 700 to 800 μEql^{-1} (Figure 6.6): either side the standard error increases. Plotting the proportion of base-flow against the proportion of base-flow plus/minus the standard error (Figure 6.6) confirms the patterns observed previously with the minimum variations at intermediate to high values of P_{base}. However, at the extreme values the errors begin to diverge from the 1:1 ratio indicating a greater uncertainty in these ranges.

The uncertainty analysis would indicate the standard error in applying the mixing model to the ANC endmembers identified for Coalburn are relatively small/acceptable; probably reflecting the well defined nature of the endmembers. However, this only reflect the variation in the samples used to define the endmembers and the variance analysis assumes the errors in the ANC estimates are small compared to the errors in the endmembers. Overall the values and results must be tempered with some caution and results from the mixing model should not be used as absolute values but rather as indicative of the processes occurring at Coalburn. These can then be used in conjunction with other evidence to validate the hypotheses set up by the runoff model.

The examination of the errors and the process of deriving the endmembers highlight the need to sample at extreme flows and that particular attention should be focused on the identification of the high-flow endmember when considering such studies.

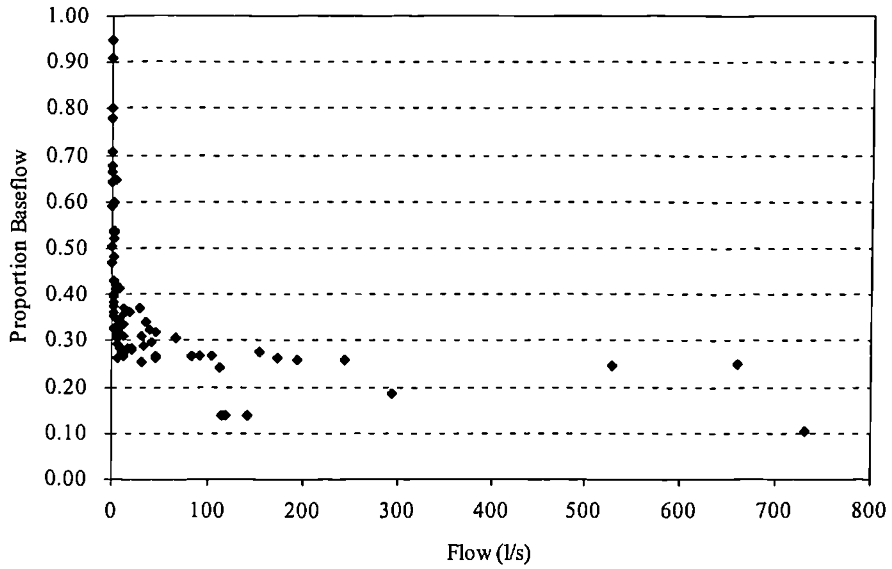
6.4.4 Endmember mixing model: spot samples

The proportions of base and high-flow water were assessed for spot sampled ANC values at the catchment outfall using the endmember values and mixing model (Equation 6.01). The flow-weighted average P_{base} was 26%, suggesting that the high-flow endmember dominates the catchment output. The P_{base} ranged from 95% to 11%, and all of the spot sampled ANC values fell in the range of the estimated endmembers. If the P_{base} value was greater than 100% it would indicate a higher base-flow endmember was required to explain the stream ANC. There were no negative values of P_{base} to suggest a more acidic endmember was required.

Applying the sensitivity analysis, by first holding the base-flow endmember constant and varying the high-flow endmember, the P_{base} ranges between 95% and 8%. Repeating the process for the base-flow endmember, the P_{base} ranges between 101% and 10%. Consequently, the P_{base} can range between 101% to 8% and these errors need to be borne in mind when interpreting the results.

The proportions of the base and high-flow endmembers vary with flow (Figure 6.7). The base-flow endmember dominates during low flow conditions and as flow increases the base-flow endmember is rapidly 'diluted' by the high-flow endmember with the relationship being approximately exponential. This confirms the hypothesis that the Coalburn hydrochemical response can be explained by catchment processes and varying proportions of the base and high-flow chemical signatures. This assumption has been the foundation of the Coalburn runoff model and discussions of the causal mechanisms (Chapter 4 & 5).

Figure 6.7 Estimated proportions of base flow for spot sampled data

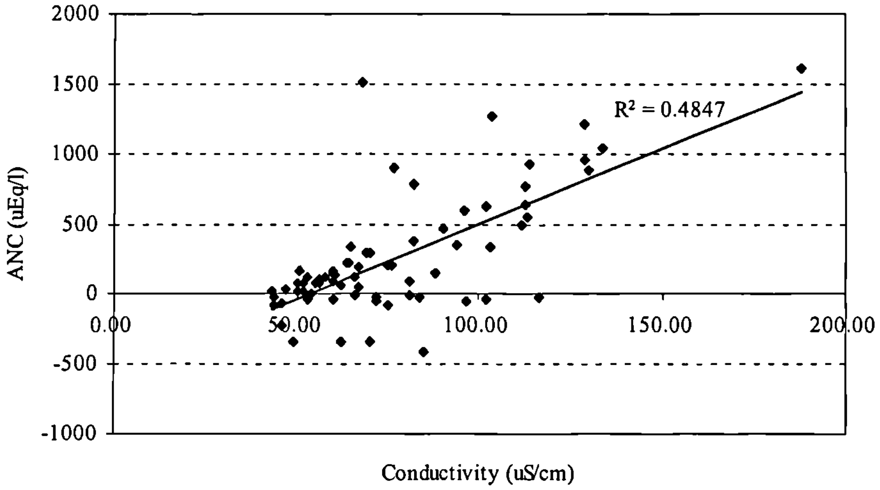


The Coalburn stream ANC exhibits a linear relationship with the stream conductivity for the spot samples (Figure 6.8). However, a similar observation is not seen between the rainfall ANC_{CBALK} (calculated as per equation 6.04) and conductivity (Figure 6.8). Robson et al. (1992) explained similar scatter in the rainfall data at Plynlimon as arising from marine inputs, showing no increase in ANC for high conductivity rainwaters whilst inputs with a terrestrial signature increase conductivity and lower the ANC. These observations provide further evidence that catchment processes dominate the Coalburn hydrochemical response, otherwise the rainfall signal would introduce more variation into the relationship.

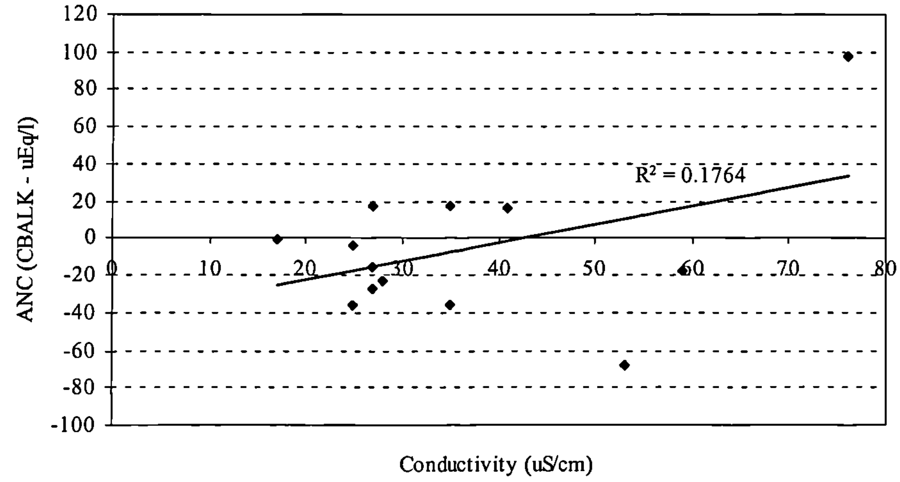
The relationship between the P_{base} and other chemical solutes follow the expected pattern. The solutes associated with the base-flow signature identified in Chapter 3 show a positive relationship with P_{base} (e.g. calcium), while solutes associated with the high-flow signature exhibit an negative relationship (e.g. aluminium).

Figure 6.8 Coalburn ANC conductivity relationships

Coalburn Stream



Coalburn Rainfall



6.4.5 Chemical hydrograph separation

To employ the mixing model during events it is necessary to produce a ‘continuous’ series of ANC values for Coalburn, which was not directly available. However, ANC and hydrogen ions (pH) are closely related (Figure 6.3) and pH can be used to predict ANC using equation 6.16:

$$\mathrm{ANC} = \{10^{[-0.00672(\log(\mathrm{H}))\verb|^|3 + 0.105928(\log(\mathrm{H}))\verb|^|2 - 0.069(\log(\mathrm{H})) + 2.75964]} - 500\} \tag{6.16}$$

Where H = Hydrogen ion concentration ($\mu\mathrm{Eql}^{-1}$)
R^2 = 0.90
N = 82
^ = To the power of.

It is now possible to model a continuous ANC time series from the $\mathrm{pH_c}$ data.

The ANC time series was derived for Events 1 to 9 (Chapter 5), and the responses display similar characteristics to the $\mathrm{pH_c}$ time series from which it was derived (Figure 6.9). The results of applying the mixing model to Events 1 to 9 are summarised in Table 6.7 and Appendices A to I, this shows the maximum and minimum values for the ANC and P_{base}.

At this stage, it is worth recalling that the Coalburn catchment hydrochemical response has been linked to the vertical gradients and strong spatial patterns. The proportions of the base and high-flow endmembers do not simply reflect the partitioning of the water into deep and soil-water but also the spatial variability (i.e. the peat and peaty-gley sub-catchment signatures) in the Coalburn catchment. These need to be borne in mind when considering the causal mechanisms that underlie the results from the mixing model.

On first examination of Table 6.7 the maximum ANC values of 3450 and 3540 $\mu\mathrm{Eql}^{-1}$ for Events 1 and 2 are immediately apparent. These are much greater than the base-flow endmember and consequently P_{base} is much greater than 100%. These events were during low base-flow periods (0.61 and 0.21 ls^{-1} respectively) and this was reflected in the elevated pH. Therefore, the continuous pH values were outwith the valid range for the pH-ANC model and so the results should be discounted as an artefact of applying the model to an invalid range. Furthermore, under low flow conditions diurnal variations

Table 6.7 Summary of mixing modelling for events 1 - 9

DAC	Event 1 19 June 95		Event 2 06 July 95		Event 3 03 July 96		Event 4 06 July 1994		Event 5 23 April 96	
	Max	Min	Max	Min	Max	Min	Max	Min	Max	Min
ANC	3450	37	3540	25	955	-31	918	68	98	-79
P_{base}	1.71	0.29	1.75	0.29	0.67	0.26	0.66	0.31	0.32	0.24

WAC	Event 6 05 Nov 96		Event 7 21 January 95		Event 8 10 Nov 95		Event 9 31 January 95	
	Max	Min	Max	Min	Max	Min	Max	Min
ANC	17	-111	38	-73	50	-87	55	-68
P_{base}	0.28	0.21	0.29	0.25	0.30	0.24	0.30	0.25

and respiration affect the pH_c measurements taken in the weir pool (Chapter 2), consequently the high pH_c may only reflect the pool effect rather than catchment processes.

There is a distinct difference between the Events 1 to 4 with Dry Antecedent Conditions (DAC) and Events 6 to 9 with Wet Antecedent Conditions (WAC) with Event 5 being transitional (Table 6.7). This validates the classification of the Coalburn events as hypothesised in Chapter 5. Typically, Events 1-4 had a high P_{base} and ANC at the beginning of the event, reflecting the dry antecedent conditions and dominance of the base-flow endmember/signature associated with deep-water and the peaty-gley sub-catchment. With the onset of an event, the base-flow endmember is rapidly diluted by the high-flow endmember resulting in a rapid decrease in the P_{base} and ANC. In most events, the ANC remained positive; however, it varied by up to two orders of magnitude.

In contrast, Events 6 to 9 initially had low P_{base} and ANC values. During the event P_{base} varied comparatively little and this is reflected in the ANC which did not fall too the same extent as DAC events, however, the ANC often became negative. One should be cautious in only considering the percentages during events as the flows involved are relatively large (compared to DAC) and a small variation in the percentage can represent large volume of water at the catchment outfall. The general pattern reflects the high antecedent saturation and the greater contribution of water from the soil zones and the peat sub-catchment, which reduce the initial P_{base} and ANC. Consequently, even though the high-flow chemical signature was dominating and large quantities of water were delivered from the soil zones and peat sub-catchment there was not a large change in chemistry at the outfall (compared to a DAC event).

In the events examined, the ANC was not reduced to the high-flow endmember (-666 μEql^{-1}) identified from site SM8. This suggests the base-flow component had an important ameliorating effect on the event intensity. Consequently, Coalburn would be sensitive to any changes in management (e.g. repeated forestry cycles that depleted the cation exchange capacity of the soils, or more complete drainage) that would modify either the quantity or the buffering capacity of the base-flow component.

The mixing model was able to explain the observed hydrochemical response, except at very low flow with high pH which was probably explained by the pool effect rather than a missing endmember. This implies that catchment processes dominate most events at Coalburn. If this were not the case then the mixing model would not be able to explain the hydrochemical response without anomalous or erroneous features being immediately apparent. This suggest that either the rainfall displaces pre-event water bearing the chemical fingerprint of the endmembers or event water is rapidly modified by catchment processes so it is indistinguishable from the endmembers (Robson et al., 1992). However, it should be recalled that the ANC is derived from the pH at the catchment outfall; the pH being rapidly modified by catchment processes. It is currently not possible to confidently state whether event or pre-event water dominates without further studies, such as isotope tracing or DOC monitoring. Other similar studies suggest that pre-event water dominates (Neal and Rosier, 1990). However, it will become apparent that this may not be the case at Coalburn, and the response may be a combination of event and pre-event water depending upon the antecedent and event conditions.

The dry antecedent event on 06 July 95 had an initial pH that was outwith the pH-ANC model and the ANC values should be discounted until pH reaches 7.50 (Appendix B). During the event, ANC fell rapidly as flow increased and reached a minimum of 42 μEql^{-1} (07 July at 1900), this lagged peak flow and was synchronous with the minimum pH_c. The ANC fell more rapidly than pH_c, however, this was probably a function of the pH-ANC model rather than catchment processes. The ANC then remained depressed and slowly recovered as the event receded.

During the early part of the event, the increase in flow was predominantly accounted for by the base-flow component, which was reflected in the relatively minor changes in the pH_c, conductivity and other chemical solutes. This implies the Coalburn hydrochemical response, at this point, could be explained by deep-water movement to the stream and/or the contribution from the peaty-gley sub-catchment (closer to the catchment outfall). As the event continued and flow increased (above 40 ls^{-1}) the proportion of the high-flow endmember (P_{high}) increased. By this time the catchment canopy and soils would have 'wetted-up' and the soil-water and peat sub-catchment would begin to contribute. The P_{high} contribution increased rapidly and this was reflected in the hydrochemical response with an equally rapid fall in pH, ANC, calcium and magnesium concentrations associated with dilution of the deep-water base-flow signature. In contrast, aluminium concentrations (associated with the high-flow signature) increased.

The first and second peak flows influenced the relative contributions of P_{base} and P_{high}; however, the overall trend was an increasing component of P_{high} and the hydrochemical response continued to be rapidly transformed to the high-flow signature.

The P_{high} maximum lagged peak flow by seven hours and represented the greatest contribution of the soil and peat sub-catchment water that resulted in a minimum in the pH_c, ANC, calcium and magnesium concentrations. This is consistent with the hypothesis that the most acidic waters do not, generally, contribute until the recession limb, although the timing is dependent on the event intensity (i.e. the speed at which the soil water and peat sub-catchment contribute). This is a fundamental factor controlling the Coalburn hydrochemical response and accounts for the pH_c minimum occurring after peak flow in most instances.

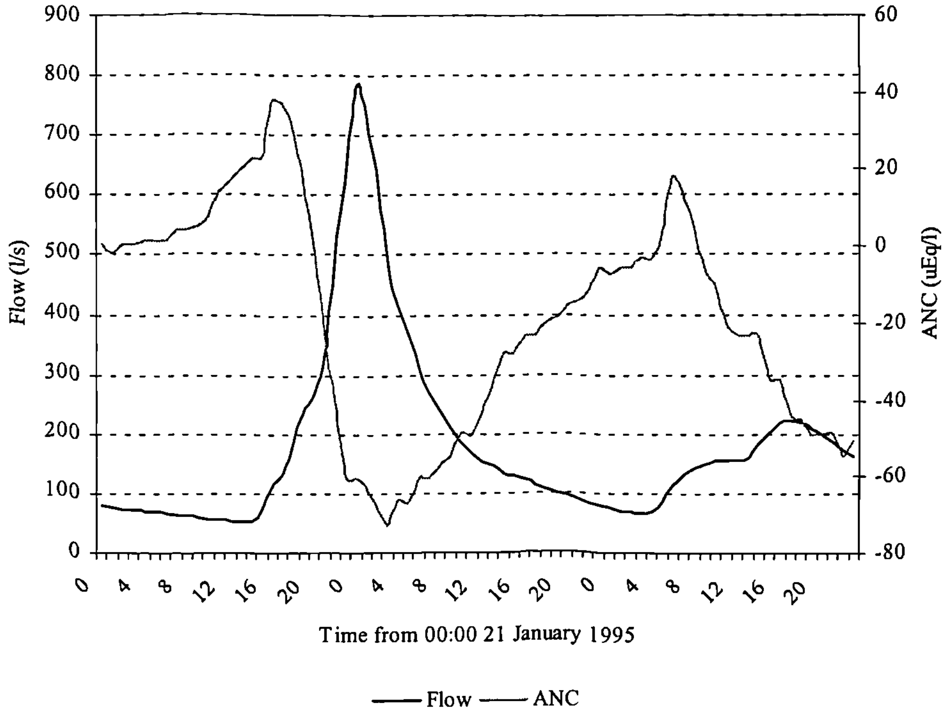
The catchment then began to recover, however, the P_{base} remained low and the P_{high} continued to contribute over 70% of the total flow for the remainder of the event. This verifies the hypothesis that the hydraulic conductivity of the peat results in the high-flow signature continuing dominate well after the event, increasing the duration of the events at Coalburn.

The DAC response was characterised by rapid and distinct change in the P_{base} which was also reflected in the other chemical solutes that are indicative of the baseflow endmember. For example, the calcium and magnesium concentrations fell during the event and these are associated with the base-flow signature. In contrast, aluminium (high-flow signature) increased during the event. The DAC response was similar to those observed in other catchments e.g. Plynlimon (Robson, 1993). There was no indication during the event that other endmembers were required to explain the observed hydrochemistry.

The wet antecedent event on 21 January 1995 had a low initial pH_c of 4.78 and an ANC value of 20 μEql^{-1}, low but still positive (Figure 6.9; Appendix G). During the event, the ANC exhibited an initial increase (similar to pH_c), rising from 20 to 38 μEql^{-1} before rapidly falling to a minimum of –73 μEql^{-1}, lagging peak flow by one hour. The ANC then began to recover slowly but the recovery was truncated by the next event.

Figure 6.9 ANC during a hydrological event

(Event 7 21 January 1995)



The mixing model indicated the P_{base} was initially low (29 %), a function of the wet antecedent conditions which meant the soil water and peat sub-catchment were volumetrically and chemically dominating the flow. This implies the event starting point is important in determining the catchment response; in this case, the catchment had not fully recovered from previous events. During the event, P_{base} did not vary a great deal (between 25 and 30%) and the change between P_{base} and P_{high} was not as pronounced as the DAC response. This is further evidence that the DAC and WAC responses are distinct in terms of hydrochemistry and processes.

During the early part of the event the mixing model explained the initial pulse in ANC by an increase in P_{base}, which must be a function of a rapid delivery of deep-water from near the channel and/or from the peaty-gley sub-catchment, as hypothesised in Chapter 5. It would seem reasonable/acceptable from hydrological principles that this could occur and it was not necessary to adopt a further endmember to explain this observation (Chapter 5). A similar process was observed in the DAC response. The initial rise in flow was ascribed to the base-flow component; however, with dry antecedent conditions this would not influence the stream hydrochemistry as the Coalburn already has a base-flow signature. This implies the causal mechanism underlying the initial pulse in ANC, pH and conductivity operates during all the events. However, it is only observed during the WAC events when it buffers the high-flow signature is dominating at the beginning of the event.

Further evidence of the initial pulse occurring for all events was observed in Event 1 (Chapter 5). During the initial phase of Event 1 there was a decrease in colour concentrations that was ascribed to a delivery of peat-gley sub-catchment water. Thus, the use of other solutes and chemical signatures may be useful in unravelling the mechanisms behind the initial pH and conductivity response and could be the focus of future work.

The ANC and P_{base} then fell as the catchment responded to the rainfall event, reflecting the delivery of more acidic waters from the soil water and peat sub-catchment. This does not reach a minimum until after the peak flow when the most acidic contributions were made in terms of the soil water and peat sub-catchment; the wet antecedent conditions appear to reduce the lag time.

Catchment recovery then began, however, the P_{base} remained low and only recovered to 28% by the beginning of the next event. This verifies the hypothesis that the low hydraulic conductivity of the peat results in the high-flow signature continuing to contribute and dominate well after the event and that successive events lead to a gradual decline in the P_{base}.

The extended duration of the acid events at Coalburn results in a progressive increase in the acidity of successive events during the winter months when wet antecedent conditions are dominant. This results in a distinct difference between the summer and winter acidity status of the Coalburn catchment (Chapter 3) reflecting the importance of the saturation status of the catchment and the dominant flowpaths, processes and sources. However, the catchment acidity does not continue to fall to the high-flow endmember. The contributions from the P_{base} and P_{high} reach a lower 'steady-state' during the winter, with the P_{base} being 20 to 30% of the flow (roughly equivalent to the proportions of peat and peaty-gley soils in the catchment). The continued P_{base} contribution plays an important role in ameliorating the acidity at Coalburn (i.e. buffers against reaching ANC of –666 μEql^{-1}). Any change in environment management that reduced this proportion would result in acidic conditions being more frequent (particularly during the winter) and the magnitude of the events would be more acute.

The wet antecedent event on 31 January 1995 had a low initial pH of 4.90 and an ANC of 28 μEql^{-1} (Appendix I). During the event, the ANC exhibited an initial increase rising from 28 to 55 μEql^{-1} before rapidly falling to a minimum of –68 μEql^{-1} one hour before peak flow. The ANC was expected to reach a minimum following the peak flow and at a much lower value given the magnitude of the flow, however, this reflects the pH_c response.

The mixing model produced a response similar to the event on 21 January 1995. However, as the event progressed, the ANC reached a minimum prior to the peak flow and then recovered. The two-component mixing model could only explain this by an increase in the base-flow endmember. However, an increase in the deep-water component or an increase from the peaty-gley sub-catchment is unlikely at this stage of an event, unless the rainfall was highly localised which is not evident in the rainfall data. Furthermore, if this were the case then a concurrent increase in conductivity would also be expected.

In Chapter 5, the response was explained by an event water component (i.e. rainfall) due to the saturated status of the catchment, the event intensity and a washout process. The mixing model work would support this theory in that a third 'event water' endmember is required to fully explain the catchment response. This is consistent with the hypothesis that the event intensity affects when the delivery of the most acidic water occurs, in this instance it is not in terms of times of travel, but amelioration from the event water component (i.e. rainfall). Indeed, during this period the continuous ANC and conductivity do not show the linear relationship observed for the spot sampled data that would suggest the rainfall signal was influencing the Coalburn response, as discussed earlier in the chapter.

Consequently, during extreme events with wet antecedent conditions a third endmember may be required to explain the Coalburn hydrochemical response. This may be a function of event and antecedent conditions, but also the density and effectiveness of the drainage ditches that rapidly transfer this water to the catchment with little chemical modification.

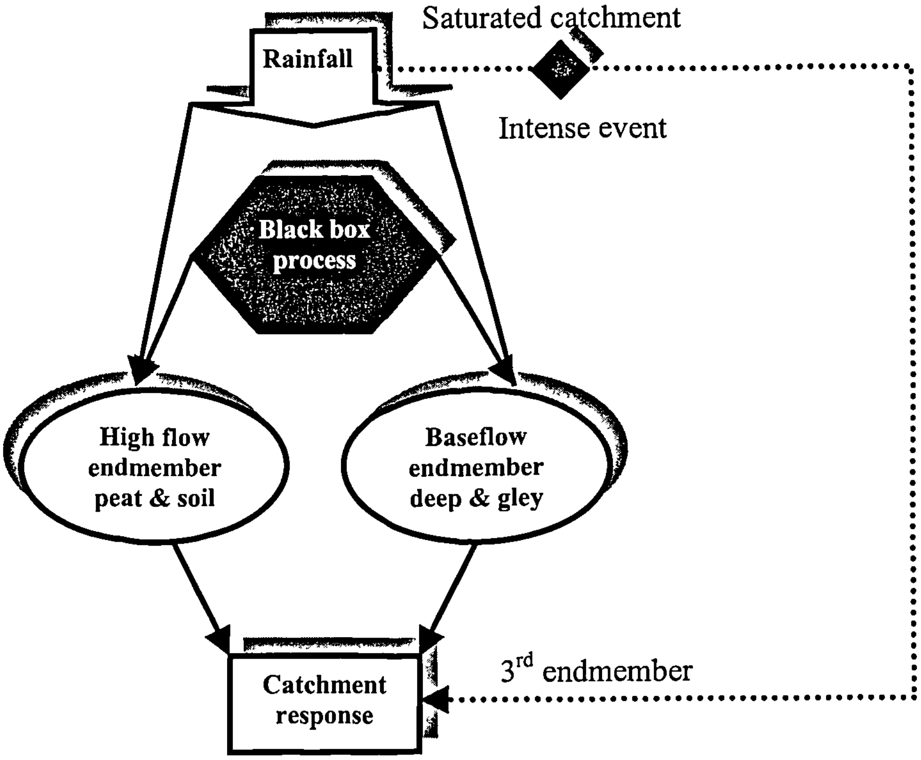
6.5 Coalburn runoff models

Results from the mixing modelling suggest the Coalburn hydrochemical response can be explained by the Coalburn mixing model (Figure 6.10), this is fundamentally similar to the Coalburn runoff model and it is encouraging the two models, derived from different conceptual origins, have produced similar results.

The Coalburn mixing model uses the hydrograph as the integrated catchment response to an event and this is partitioned into the base or high-flow endmember by a 'black box' process. The mixture of these endmembers then explains the hydrochemical response. When an extreme event occurs on a saturated catchment a third 'event water' endmember then comes into play and affects the Coalburn hydrochemical response, although this still needs to be defined.

Comparing the two models, the fundamental difference is that the Coalburn mixing model assumes that the within catchment processes fully explain the hydrochemical response, except during times of heavy rainfall when a third endmember comes into play. The effects of antecedent pollution history and vegetation are not distinct components of this model, however, their effects have already been integrated into the identified endmembers. While the Coalburn mixing model appears superficially simpler and retains good explanatory powers, the assumptions that underpin this model should not be forgotten (section 6.1.1). In contrast, the runoff model appears more complex and over parameterised, a common criticism of the hydrological models (upon which it was based) (McCulloch, 1997). However, there are no underlying assumptions other than first hydrochemical principles.

Figure 6.10 Coalburn mixing model



The compromise is to combine the two models and this produces the Coalburn Model (Figure 6.11). Conceptually the model operates as follows: for a given event, the rain will enter the catchment and in doing so may be modified by the antecedent pollution climatology. Under normal conditions, the rainfall will enter the canopy (grass and tree). However, if the catchment is saturated the rainfall may enter one of the enlarged mires/floodplains that have reached saturated excess and by-pass the catchment soils (i.e. event water contribution).

Once in the canopy the rainfall is partitioned to stemflow or throughfall, this can then enter the catchment soil. Again, under certain conditions (dry or saturated catchment) the stemflow and throughfall signal can short-circuit through or over the soils and contribute directly to the drainage ditches and the catchment outfall (event water).

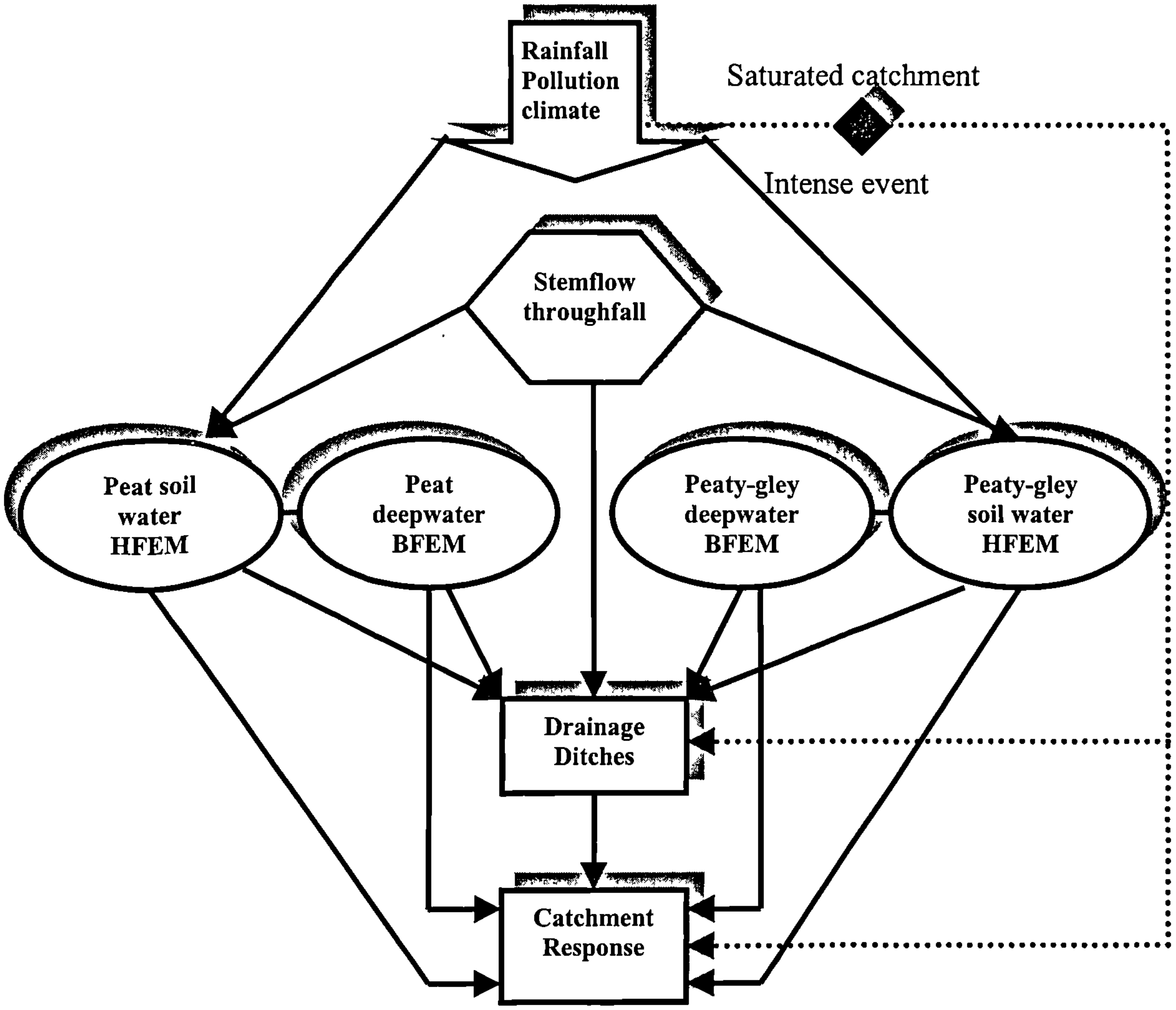
The stemflow and throughflow that enters the soil will, depending on its flowpath and residence time, pick up either a soil/peat sub-catchment signature indicative of the high-flow endmember or a deep/peaty-gley signature that is indicative of the base-flow endmember. This forms the pre-event water store that dominates the subsequent hydrochemical response at Coalburn (i.e. it is the largest water source).

During base-flow periods the low hydraulic conductivity of the soils (Waterfall, 1994; Baglee, 1994) imply the pre-event deep-water component must seep to the drainage ditches and main channel, as evidenced by the presence of ochreous deposits (or through a process of upwelling on the peat catchment). Furthermore, in the peaty-gley sub-catchment the pre-event deep-water travels slowly along the preferential pathways that result from slumping/cracking. Both of these flowpaths result in the characteristically well buffered base-flow chemistry observed in Coalburn.

During events the pre-event high-flow signature dominates and is derived from upper solum throughflow. However, this signature can be modified and/or overwhelmed by event water by the mechanisms discussed above.

The conceptual model has given an understanding of the casual mechanism behind the Coalburn hydrochemical response. In addition, it should be recalled that the antecedent moisture and pollution climatology controls the starting point of an event and the event intensity controls the rate at which the processes occur. All these factors vary infinitely in the environment, however, the conceptual model gives a simple framework to understand the process operating.

Figure 6.11 The Coalburn model



Key

…………… 3rd endmember

BFEM Baseflow endmember.

HFEM Highflow endmember.

6.6 Summary

A mixing model approach has successfully been applied to the Coalburn data and this has produced valuable information on the flowpaths and residence times in the Coalburn catchment. However, this must be tempered against the uncertainties inherent in the derivation of the ANC and endmember values:

- The base-flow endmember was inferred from the base-flow signature, this might not be truly representative of the groundwater endmember.

- The high-flow endmember exhibits significant spatial and temporal trends and may not represent the high-flow endmember for the whole catchment.

A range of ANC values were used for the endmembers in the mixing modelling to take some account of these uncertainties. The error in the actual application of the mixing model using the endmembers was relatively small, probably reflecting the well-defined nature of the endmembers.

Application of the mixing model to the Coalburn data has confirmed that at least three distinct sources of water are required to explain the Coalburn hydrochemical response (Figure 6.10). This is consistent with the observations in previous chapters.

In summary, the mixing modelling showed:

- The flow-weighted average P_{base} was 26%, implying the high-flow endmember dominates the catchment output. The dominance of high-flow signature may reflect the low hydraulic conductivity of the peat (i.e. events prolonged) and/or the drainage ditches that still influence the catchment storage by promoting rapid runoff during events. These are consistent with the hydrological observations made by Mounsey and Newson (1995) and Robinson et al. (1998).

- The relationship between the P_{base} and the chemical solutes associated with the base-flow and high-flow signatures (Chapter 3) are consistent.

- The mixing model exhibits distinct differences between the DAC and WAC events i.e. the event starting point is fundamental in determining the catchment hydrochemical response and processes.

- The base-flow component has an ameliorating effect on the event intensity and magnitude; any changes in management that would exclude or reduce this component would have a detrimental impact on the Coalburn hydrochemistry.

- The initial pulse during a WAC event was explained by the mixing model as a function of a rapid delivery of deep-water from near the channel and/or from the peaty-gley sub-catchment. The process occurs in all events, but is only observed during WAC events.

- The most acidic waters do not contribute until the recession limb, although the timing is dependent on the intensity of the event.

- The Coalburn hydrochemical response can broadly be explained by catchment processes and varying contributions of the base and high-flow chemical signatures, however, during extreme events with wet antecedent conditions a third event water endmember was required. This suggests that under most conditions the rainfall displaces pre-event water bearing the chemical fingerprint of the endmembers, while during extreme events a component of event water is introduced.

- The hydraulic conductivity of the peat prolongs the duration of acid events at Coalburn.

- The extended duration of the acid events at Coalburn results in a progressive increase in the acidity of successive acid events during the winter months, when wet antecedent conditions are dominant. This results in a distinct difference between the summer and winter acidity status of the Coalburn catchment.

- The Coalburn Model has conceptualised the hydrochemical response and combines features from the Coalburn mixing model and the Coalburn runoff model, and it would appear to provide a reasonable framework to predict the hydrochemical response at Coalburn.

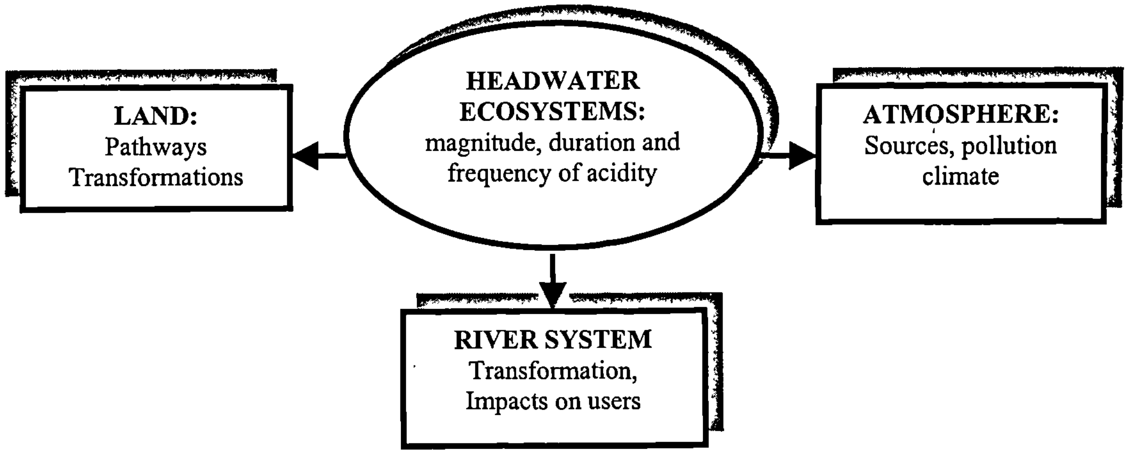
7 Coalburn: Relevance of the acidification study to public policy and the Environment Agency operations

Overview

The studies reported here have contributed to the understanding and calibration of the temporal and spatial variability (and hence risks) observed in the processes operating in upland catchments, such as Coalburn. These may be regarded as scientific contributions to decision support, but the information gathered at Coalburn has even more direct application in the field of general environmental policy and, in particular, to the operations of the Environment Agency in controlling/monitoring pollution and managing aquatic ecosystems in a sustainable manner, especially in vital headwaters.

The simple diagram Figure 7.1 reveals the potential contributions in three main directions 'out' of the headwater ecosystem and there are, of course, obvious applications within headwater stream management. These routes of application are considered in this Chapter. The chapter also explores the policy implications and approaches the Environment Agency could adopt to manage acidification in headwaters; including a headwaters appraisal strategy and the costs that this could involve.

Figure 7.1 Headwater research and management



7.1 Atmosphere

The critical load approach to controlling acid emissions at source has now become firmly implanted in the UK and EU policy. Critical loads were defined by Nilsson and Grennfelt (1988) as:

> *'A critical load for acid deposition is the highest deposition of acidifying compounds that will not cause chemical changes leading to harmful effects on ecosystem structure and function.'*

The system models the average atmospheric loading to terrestrial soil and water systems (on a grid-square basis) and compares this with the sensitivity of that system. It then becomes a political objective to reduce the loading below that critical for the system's healthy functioning. This is a more rounded approach than simple toxicity testing, as used in assessing the pollution impacts of point sources of conservative chemicals. It can be used for broad target setting and the Forest and Water Guidelines (3rd Edition) recommend that catchment based assessments are likely to be required for new proposals of plantation forestry where critical loads are exceeded.

There are uncertainties in the critical load approach and these are summarised from Battarbee et al. (1995):

Primary data The critical load depends on the quality of the primary data especially site selection, the representivity of the single sample collected, the accuracy of the chemical analysis and the validity of the assumptions in the model. Other issues include:

- Was the water sample in the grid square representative?
- Has the choice of standing waters rather than streamflow influenced the results?
- Where headwater streams were used, what effect did the chemistry-flow relationship have on the results?

Nitrogen deposition The critical loads approach assumes sulphur is the main acidifying agent, however, in some catchments significant quantities of atmospheric nitrogen (and ammonium) are deposited (e.g. Coalburn). Indeed, in some areas critical load exceedence may be driven by nitrogen deposition alone, especially Cumbria, implying reductions in sulphur deposition alone will not be enough to protect the ecosystem (Stevens et al., 1997b; Department of the Environment, 1994; Hornung et al., 1994).

Reversibility and biological recovery The critical load approach assumes the ecosystems degraded by acid deposition will recover as emissions and hence deposition decrease. From the biological perspective, the recovery is assumed to be dose-response related i.e. a recovery of increasing magnitude will result for greater reductions in emissions. However, evidence suggests the reversibility of acidification is more complex and dependent upon sulphur absorption and desorbtion characteristics in the catchment. Consequently, future land-use and nitrogen emission reduction strategies may need to be considered (Battarbee et al., 1995).

The Coalburn research indicates that caution is needed in assuming good spatial and temporal resolution for the critical loads approach. Within one small catchment there are at least two clear ‘domains’ that generate runoff of different acidity. Furthermore, there is a complex combination of climatic and hydrological conditions through time that make the true loading to the freshwater ecosystem virtually unpredictable without extensive real-time monitoring of water quality parameters that are linked to the 'target' organism by a dose-response relationship. Whilst it would be possible to use the pollution climate of Coalburn (i.e. the relationship, eluded to here, between airflow and acid inputs), it is essential that biologists assess the true sensitivity of the organisms at risk before the fine detail of the impacts can be used for management (Gee & Smith, 1997). The Environment Agency needs, when commenting on forest management proposals, to have this deeper understanding of the spatial and temporal extremes that can characterise acidification in headwaters and the resilience/sensitivity of the ecosystem (or 'key' species). The critical load maps provide a screening tool to identify the areas of concern and prioritise those sites that are at risk. If a development is proposed on a sensitive site then an appropriate catchment assessment is essential, as per the Forest and Water Guidelines (Forestry Authority, 1993).

While the critical loads approach has been effective in reducing non-marine sulphate deposition, the increase in nitrogen emissions, particularly from cars, implies the effects of nitrogen deposition need to be considered when appraising an ecosystems' sensitivity (as do nitrogen emission reduction strategies).

Coalburn receives elevated nitrate and ammonium concentrations in wet and cloud mist deposition; however, it would appear that nitrogen saturation has not occurred as these solutes are not evident in the stream chemistry. This should be tempered with the knowledge that there were no measurements of dissolved organic nitrogen in the stream (which can be significant in peat catchments). As the forest ages and the canopy area increases to its maximum, it is likely to become more effective at scavenging from the atmosphere. This will be at a time when the forest will use less nutrients (Stevens, et al., 1997b; Van Miegroet, 1994; Emmett et al., 1994; and Department of Environment and Forestry Commission, 1990). Hence, there is a risk of nitrogen excess occurring. The risk of nitrogen excess could be exacerbated by climate change, which could increase the mineralisation of nitrogen in the soil. Thus, the nitrogen status of the ecosystem and the biological activity inherent in the timber production process is important in determining the likely effects of atmospheric deposition (particularly nitrogen) on the catchment acidification status (Davies et al., 1992).

The above discussion clearly demonstrated that the effects and role of the atmosphere change in time and space and is an important component to consider when carrying out a catchment assessment. Furthermore, it highlights the importance of having long-term studies to be able to assess and quantify these changes.

7.2 Headwater ecosystems

The Coalburn research has established a finely resolved duration, frequency, magnitude relationship for streamwater acidity (Figure 4.2). When compared with parallel surveys of biota (Prigg, 1994; Prigg, 1999; Appendix J) it reveals the likely process by which the broadly toxic effects operate at Coalburn.

Biological and fish surveys have indicated an impoverished invertebrate fauna at Coalburn, vulnerable to enhanced acidification by coniferous afforestation according to the classification system developed by Rutt et al. (1990) relating invertebrate fauna to stream chemistry. The invertebrate status at Coalburn has not changed between 1993 and 1998 (Prigg, 1994; Prigg, 1999). Brown trout are present in Coalburn and in comparison to other acid stressed streams in Cumbria, they are not pathologically low in numbers. Comparisons between the 1993 and 1998 surveys reveal a decline in the trout population that may be partly a function of the population's isolated status (i.e. upstream of the flow measuring weir). Stresses that could have affected this isolated population and caused the decline include low flows and predation, as well as acid stress at sensitive life stages, however, the unchanged invertebrate status would suggest the latter is unlikely. The seasonal bias in the acidification is highly relevant at Coalburn: during winter the invertebrates may 'dig in' to the hyporheic zone of the stream and in doing so may be less affected by the more severe acid events. During the summer (invertebrates more active) the acid events are less severe.

The Coalburn studies have demonstrated that the linkages between landuse and biological/chemical impact are not straightforward and an understanding of the local conditions is required before the response can be understood. Another example of this is presented by Gee and Smith (1997) who studied invertebrate populations in the headwaters of the Wye and Severn before and after felling. The clear felling resulted in physical and chemical changes in the streams but there was no change in the invertebrate populations.

The Coalburn studies have, through their breadth, also allowed a fuller picture of the chemical quality of upland water, yielding valuable information which allows the assessment of the risks of exceeding EQS and/or critical ecological thresholds (Chapter 4). The magnitude, frequency and occurrence of the aluminium and hydrogen ion concentrations would appear to be toxic (Chapter 4), yet, there is no observable evidence of an acute impact on the aquatic ecosystem (Prigg, 1994; Prigg, 1999).

Organic acids derived from the peat soils have been identified as being an important source of acidity during acid events at Coalburn. However, the effects of natural acidity are not always detrimental, Havas et al. (1984) and Kullberg et al. (1993) suggest that brown waters have a greater ANC than similar clear water system when the pH < 5. The greater buffering capacities of brown waters can affect the frequency and duration of acid events. However, while this characteristic can slow the pH depressions it can, by the same token, slow recovery due to the hydraulic conductivity of peat (e.g. Coalburn).

The biotic effects of acidification are modified by the presence of dissolved humic compounds that reduce the toxicity of dissolved metals. For example, aluminium in brown waters is generally not in the toxic labile (inorganic) species as with clear water acidity (Driscoll et al., 1988). However, this aluminium may become toxic at low pH (Kullberg et al., 1993). Consequently, for the same acidic pH, brown waters have a greater species richness than their clear water counterparts (Havas et al., 1984; Kullberg et al., 1993). Hence, when predicting the effects of acidification upon headwater ecosystems it is important to identify the source(s) of acidity (how to go about such an assessment is discussed further in section 7.6).

For Coalburn, the absence of an acute effect on the aquatic ecosystem (Prigg, 1994; Prigg, 1999) can be ascribed to the organic nature of the acidity, combined with the high calcium concentrations derived from the underlying geology. Thus, Coalburn, and other similar headwater ecosystems, would be sensitive to any change(s) in management that reduced these ameliorative factors, or if development were to take place where these factors were not present.

Increasingly, in addition to the critical loads approach, direct biological survey is being employed to classify upland streams and to assess the impacts of acidification (see Gee and Jones, 1995). Without the finely resolved picture of the duration, frequency and magnitude of acidification established here, no biotic measure of impact can be successfully translated into an assessment of environmental risk (through changes in land use, land management or emission controls). The Environment Agency needs to be aware of the requirement for this level of hydrochemical data for use in conjunction with its biological surveys to fully assess upland headwaters prone to acidification (discussed further in section 7.6).

7.3 Land

Much of the impetus and momentum for hydrological studies at Coalburn and other similar studies has been to inform the debate between water resource managers and foresters about the impact of commercial afforestation and the management of the crop cycle on headwater catchments. Hence, any new data, particularly at the critical stage of canopy closure, can potentially support the dialogue established via the successive volumes of the 'Forest and Water Guidelines'.

The data gathered by this study have a particular relevance to the performance of drainage ditches and non-forested riparian zones. These features have now been related to the hydrological pathways within the catchment; clearly neither a drain nor a 'buffer' zone has any relevance to outflow acidity if it is not a contact zone during a particular event. It was possible to isolate the type and components of a streamflow event for which the features of catchment management significance become operable and, therefore influence the resulting water quality. In terms of the precautionary principle, this tells the environment manger how many risks there are to cover.

At Coalburn it has been shown that a non-planted riparian zone plays little beneficial effect because of the soil's low permeability and the fact that the zone is crossed by drainage ditches (which would not happen with current forestry practice). Furthermore, the riparian zone is dominated by peat soils and an increased residence time in this zone may not be of benefit, as it could increase the acidity. It has also been shown that the artificial drainage ditches, particularly on the peat sub-catchment, still deliver acidified runoff rapidly to the catchment outfall. This demonstrates the long lived effects of the land preparation phases; even after 27 years the effects of ploughing are still evident in the Coalburn response. It is impossible to manage the land on a real time basis but such information can aid the evaluation of risk and the need to apply the precautionary principle in sensitive catchment, for example at Coalburn:

- Reduced ditching in a catchment could reduce the duration of pH below 4.0 without significantly reducing the forest yields.
- Routing of the acidic peat and the peaty-gley sub-catchment water to mix and neutralise each other could be considered.
- Boreholes could be used to manipulate the ground-water contribution as per Neal et al. (1997a) at Plynlimon.
- Catchment or stream liming remedial measures could be used as per Comber et al. (1999) at Llyn Brianne.

However, implementing these water quality management strategies/options need to be considered within a holistic approach to catchment management as they may have implications for the catchment hydrology and water resources. Also, the risks and benefits of these options need to be considered (Newson, pers. com).

Whilst the spatial hydrochemical detail is not sufficient to examine the chemical transformations occurring at every node in the hydrological cycle, the data presented here has highlighted:

- The variations in acidity status and sensitivity that can occur in a small catchment, these may not be identified from the critical loads maps; assessments at a smaller scale may be required, particularly for areas where the critical loads are exceeded.
- The B-horizon of the peaty-gley soils plays a major buffering role in the acidity observed at Coalburn. Access to this horizon is perhaps facilitated by tree roots, although more study is required.
- The artificial drainage network facilitates a third hydrochemical endmember, postulated as event water, that ameliorates the effects of acidity during extreme hydrological events.

- In a catchment such as Coalburn the flow pathways, contact zones and residence time are fundamental to the duration, frequency and magnitude of acid events.
- In comparison with other studies, the study has demonstrated the effects of afforestation vary in type and magnitude through time. The whole life impacts (positive/negative) should be considered, including successive rotations, when deciding on whether to afforest a sensitive catchment.

The information presented here adds to the understanding of the processes that operate in forested ecosystems, enabling the cause-effect-risk to be calibrated and informed decisions to be made on policies such as the Forest and Water Guidelines.

7.4 Rivers

The offsite impacts of acidification are seldom the focus of scientific analysis; downstream buffering is assumed to occur since lowland high order streams seldom suffer from profound acidification. The Environment Agency have nine key environmental themes that include integrated river basin management; improving fisheries and conservation; improving air quality; and climate change. Concern for these and regulation of surface waters ensures that headwater quality is of wider relevance than those ‘smaller’ communities who rely on the water directly (communities including humans, flora and fauna).

The hydrochemical performance of each river system is likely to be unique. However, the knowledge of temporal and spatial viability of headwater inputs allows prediction and calibration of the likely extent of failure to comply with EU and UK standards (e.g. Freshwater Fisheries Directive and the River Ecosystem classification scheme). In considering the downstream effects, the role of impoundment in the catchment system is also important. Acidification in the supply catchments of upland reservoirs may result in release of poor water quality in the reservoir, thus creating a much greater downstream effect than a natural catchment.

The importance of the faunal richness of headwater streams and their role in maintaining the diversity of the whole river catchment has been highlighted by Furze et al. (1991; 1993; 1995) and Furze (1995). Furthermore, headwaters are the breeding grounds for many fish species, including economically and ecologically valued one. Consequently, changes in the water quality may affect the downstream 'biological signal' in the reduced magnitude or diversity of migration. These issues have an economic as well as conservation value and forestry/land use issues in these upland headwaters need to be thought of in terms of risk-benefit for the entire catchment.

Acid events have been clearly identified at Coalburn, however, they have not been observed at downstream monitoring sites on the River Irthing, although the monitoring at these sites are only spot samples that can, as seen above, miss episodic acidification. However, the cumulative effect of managing several the headwaters in the same way must be considered. The River Irthing is designated as part of the River Eden catchment Site of Special Scientific Interest (SSSI) and a candidate Special Area of Conservation (cSAC) to just upstream of Gilsland (NY 6485 6980). This is by virtue of the River Irthing being host to the following species listed in the EC Habitats and Species Directive (92/43/EEC): water-crowfoots; Atlantic salmon; bullhead; river and brook river lamprey; and otters.

Consequently, changes to the management of the headwater streams which could cause an impact on the downstream water quality (in turn affecting the success of these species) would require an appropriate assessment under the Habitat Directive. With this in mind many of the listed species are sensitive to changes in the stream acidity.

The River Irthing also has commercially important salmonid populations and The Eden Salmon Action Plan has set targets to improve these fisheries based on egg deposition (Environment Agency, 1997). However, acidification could affect compliance with these, and other, standards. Compliance with such standards could be frustrated further due to the water quality changing during different phases of land-use cycles; for example, compare the step change in chemistry of a stream pre- and post-felling (Neal et al., 1992). Such variation needs to be calibrated in terms of the likely change; the longevity of Coalburn study offers the opportunity to do this by following the chemistry changes throughout the forestry cycle.

7.5 An integrated approach

The potential issues arising out of managing acidification in headwaters was summarised in Figure 7.1, and the complexities of the individual issues were discussed above. It is clearly apparent that when considering the potential impacts of acidification on the aquatic ecosystem the effects extend downstream to include the whole catchment and 'laterally' across all Environment Agency functions and to external bodies. The challenge is to integrate these requirements with the cost-benefit component into a coherent management policy to protect against the ecologically potent anthropogenic acidification (Figure 7.2). However, this is not simple and the complexity of acidification processes and difficulty in predicting the impacts implies the precautionary principle and a 'risk-benefit' approach to management has to be adopted

An acidification policy also needs to incorporate temporal flexibility to adapt to the fact that the magnitude, direction and requirements of the components can change in time and/or space (Table 7.1). Consequently, the success of shorter-term management strategies such as the salmon action plans and water quality objectives need to take into account these temporal variations.

Figure 7.2 Acidification management policy

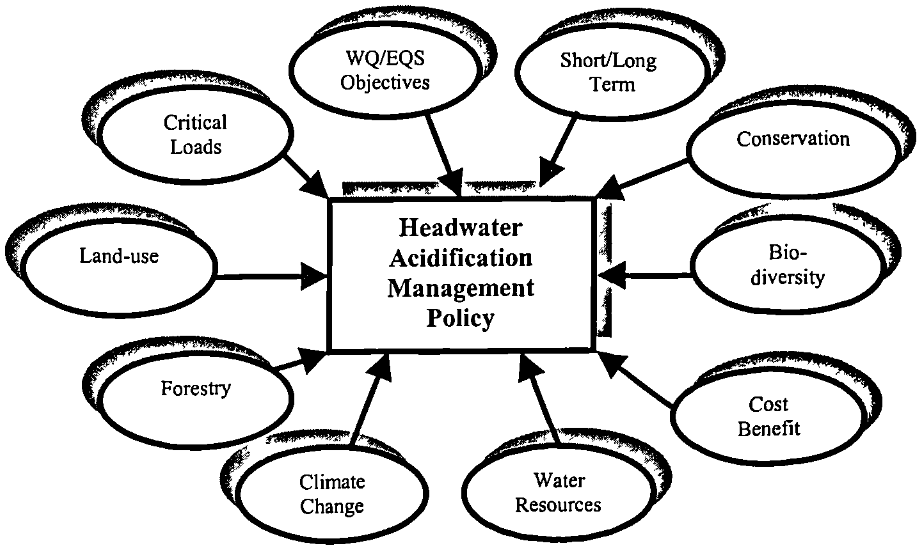


Table 7.1 Acidification and management policy: temporal issues

Component	Short Term (0 to 5 years)	Medium Term (5 to 50 years)
Forestry	Felling/afforestation and a step change in catchment processes and characteristics.	As forestry cycle progresses the magnitude and direction of effects change. Consider the effect of repeated crop rotations such as base cation export and reduction in soil CEC.
Climate change	Continued climate change marginally affect process operating in the catchment. Controls and policy to reduce the effects of climate change.	
Critical Loads	Over the next five years it is expected that sulphur deposition will decrease to 2003; this will have an impact on the critical load and catchment sensitivity to acidification.	Nitrogen deposition control strategy.
Water Quality Objectives	Water framework Directive. Standards will continue to tighten	
Conservation/ Bio-diversity	Full implementation of Habitats Directive. Value of headwater ecosystems recognised.	

One of the fundamental Environment Agency strategy documents that would lend itself to the development of an acidification strategy is the Local Environment Agency Plan (LEAP), the successor to the catchment management plans. The LEAP document is based on a catchment scale, is multi-functional and is carried out in consultation with other key parties; i.e. it is at an appropriate scale and consults the 'right' people and organisations. Typically, the LEAP could be used to identify the significant components (Figure 7.2) of an acidification issue in a catchment, for example:

- Identify the catchments that are acidified or at risk of being acidified from the critical load maps or identify catchments where more detailed critical load assessments are required.
- Identify if the ecosystem contains species that warrant special protection and are impacted by or are at risk from acidification. Similarly, the LEAP should delimit water supply resources at risk (or currently suffering) from acidification.

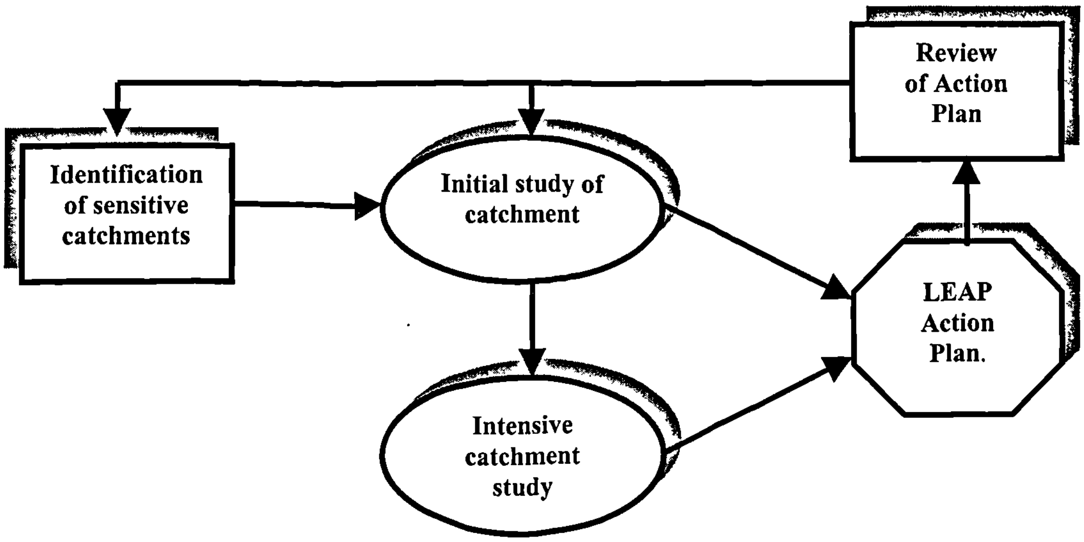
- Identify watercourses that are currently failing UK or EU water quality standards because of acidification, and those that are at risk of failing.
- Liaison and partnerships. The Environment Agency is not a statutory consultee regarding afforestation projects, however, the location, scale, nature and timing of afforestation are of prime interest to the Environment Agency. Indeed the Forest Authority's Forest and Water Guidelines (1993) encourage consultation with the Environment Agency. The LEAP would be an ideal vehicle to formally develop partnership, liaison and consultation procedures at an early stage that would help facilitate the mitigation of avoidable impacts of a proposal.

Many of the components in the acidification issue (Figure 7.2; Figure 1.1) are spatially referenced and could be analysed using a Geographic Information System (GIS). Using GIS would allow each component (Figure 7.2; Figure 1.1) to be overlaid to identify those areas in a catchment at the greatest risk. Having identified the sensitive catchments, these would require a more detailed appraisal of its sensitivity; a method is discussed in Section 7.6).

Once the true sensitivity of the relevant catchments was determined the LEAP would then identify the options for managing the catchments 'at risk' of becoming acidified, whether through new developments or established forests. The established forests refers to the potential legacy of sites in a catchment that could develop acidification problems as the forest ages and nitrogen excess occurs or successive rotations reduce the soils buffering capacity. The LEAP action plan would include a policy statement on activities, such as forestry, on sensitive catchments and future management of current sites. This would be in line with current Environment Agency policy; legislation and the Forest and Water Guidelines. One benefit of the LEAP is that it is reviewed on an annual basis and can therefore accommodate the issue of temporal variation (Table 7.1). A summary of this process is shown in Figure 7.3.

However, it should be realised the LEAP process is not the panacea. It serves a complex catchment and issues such as climate change and critical loads (e.g. nitrogen deposition strategy) require national and international policies. Furthermore, research, such as that at Coalburn, needs to continue to provide clear technical and scientific information to inform the debate over cause-effect-risk, best practise, so as to form the building blocks for future policy and future editions of the Forest and Water Guidelines.

Figure 7.3 Headwater management strategy



7.6 Acidification and headwater appraisal strategies

To adopt the above approach (Figure 7.3) there is a pre-requisite of good information and monitoring. However, water quality, biological and habitat research and monitoring has typically focused on the lowland ecosystem (Furze et al., 1991; Hind, 1992). Consequently, there is a dearth of knowledge on the headwater ecosystems and instrumented catchments such as Coalburn are the exception rather than the norm. The importance and sensitivity of the headwater ecosystem have been recognised and where a catchment is deemed sensitive to a proposed development or a current operation there is likely to be a requirement to appraise the ecosystems to fully assess the risk.

The Coalburn data have provided a full catalogue of the duration, frequency and magnitude of the short-term changes and concentration levels. It provides extensive information about the probability distributions of the determinands, and eliminates the need to fit a statistical distribution to a limited number of spot-sampled data in order to examine the extreme properties. Furthermore, an extensive sampling programme has built a chemical data-base for most elements of the Coalburn hydrological cycle; allowing the discussion of catchment processes.

Data collection for research programmes such as Coalburn have high costs in terms of capital (i.e. equipment) and operation (i.e. maintenance and analysis to give good quality data). Approximate costs for the Environment Agency's contribution to the Coalburn research programme are presented in Table 7.2. The total capital costs were estimated from the 1993 catchment refurbishment; unfortunately, costs for each of the elements were not available. It should be remember, firstly, that the Environment Agency contributions (Table 7.2) are for the total research programme, not just the water quality studies. Secondly, that the Coalburn experiment is a collaborative research programme and contributions (financial and intellectual) from the other research partners are important:

• Institute of Hydrology	Canopy interception experiments etc.
• Forest Commission	Cloud mist collectors etc.
• North West Water Ltd	Auto-sampler etc.
• Newcastle University	Calibration of pH and conductivity probe etc.

Table 7.2 Coalburn water quality research programme Environment Agency costs

Capital Items		**Estimated Cost**
Broad crested V notch weir structure Instrumentation housing Logger, shaft encoder and telecom line Chart recorder pH and conductivity probe and analyser Automatic weather station and tipping bucket raingauge		**£150 K**
Annual operational items	**Number per annum**	**Estimated cost (£ K)**
Routine samples for chemical analysis (river, rainfall and cloud mist).	72 @ £ 20 per sample.	1.44
Biological sampling and analysis	6 days	0.9
Data collection	24 days	3.6
Data validation	12 days	1.8
Data analysis and reporting	30 days	4.5
Total annual operational costs		15.24

Assumed that staff costs are £150 per day.

The aim of the Coalburn experiment is to determine, in detail, the hydrological effects of upland conifer afforestation (including the water quality element) and by its very essence is a long-term research programme. The longevity is what sets experiments such as Coalburn apart from many of the short-term (cheaper) studies. However, the expense of long-term experiments can be offset by the fact that they are essential to calibrate the short-term studies that may otherwise may make incorrect conclusions by, for example, only observing part of a cycle (McCulloch, 1997).

Given the costs involved in a research programme such as Coalburn it would not be feasible to study every headwater in the same way. Indeed, it is not necessary as the requirements and objectives of a headwater appraisal are very different from those at Coalburn:

Objective of headwater appraisal:

> 'to assess catchment sensitivity to acidification in light of a development such as afforestation'.

Nevertheless, the data gathered in the Coalburn research programme can be used to elucidate on the expected characteristics of water quality variations in headwater ecosystems and aid the design of monitoring strategies to assess the risks and effects of a development.

Recalling the discussions of the previous chapters, several components need to be considered in a catchment appraisal (however, it is difficult to be prescriptive in the appraisal design as the funds available, effort expended in the assessment and objectives should be consummate with the site importance and potential risks).

The first step is an initial study that involves a desk exercise to review the available information including critical load exceedence, presence and absence of sensitive species downstream, water quality data, geology and soils etc. The initial study should also include a field assessment to map the streams, soils and vegetation of the catchment to validate the sub-catchments and spatial variation identified in the desk exercise. Within each sub-catchments a biological assessment should be carried out to identify if the fauna is impoverished due to acidification. A chemical survey at the same points should be carried out during wet weather (preferably winter with wet antecedent conditions – worst case) with the samples analysed for the determinands in Table 2.4 to assess the chemical acidity status of the catchment.

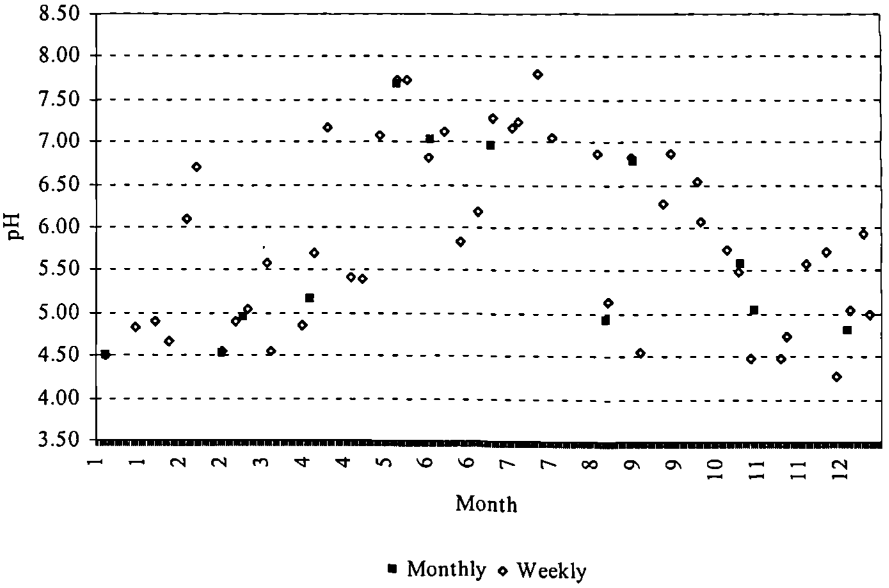
This initial study is an essential first step and it may reveal there is no risk or that it is acceptable and that no further action is required. Where further appraisal is required the initial study indicates the likely nature of the problem and can be used to direct the right amount of resource to a fuller catchment appraisal.

The cornerstone of a more detailed catchment assessment is the collection of hydrometric data. It is now relatively easy to set up and calibrate a temporary flow monitoring station to record stage on at least an hourly basis using a pressure transducer and a rated section. However, where resources do not allow a flow calibration to be derived then logged level data would suffice as an absolute minimum.

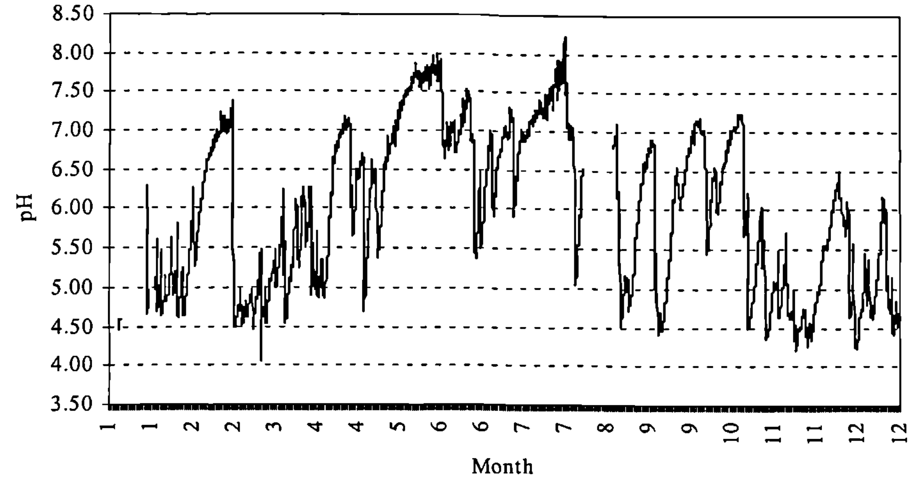
Routinely the Environment Agency samples streams and rivers 'randomly' at a monthly frequency, however, this is unlikely to capture the episodic variations in chemistry in headwater catchments (other than by luck). Figure 7.4 shows the continuous pH_c trace for 1994 and a random monthly and weekly sampling programme (limited to Monday to Friday 0900 – 1700). It can be clearly seen that a sampling programme alone is unlikely to capture the variation, except at a frequencies which are not practical. Despite this routine monitoring has a place in a catchment appraisal to identify the baseflow signature and a sampling frequency of twice monthly has worked well at Coalburn.

The identification of the high flow signature and episodic hydrochemical characteristics of a stream requires a more intensive approach. The Coalburn study has utilised continuous pH and conductivity measurements, however, these are costly and manpower intensive in terms of equipment, maintenance and data analysis (Table 7.2). Furthermore, a sampling programme is still required to derive the corrections for the pH and conductivity probes due to streaming errors etc (until better equipment is available). The continuous monitors can only furnish details of pH and conductivity (with current probes on the market) and these are only two of the parameters that are of interest for an acidification study. At Coalburn, the relationship between DOC, aluminium and calcium has been important in explaining the Coalburn response and the linkage between the chemical and biological response.

Figure 7.4 pH sampling strategies



Continuous pH 1994



In this situation the high flow signature would be better identified by the deployment of an auto-sampler sampling at a frequency between 1 - 3 hours with the capacity to sample for 48 hours analysed for the solutes as per Table 2.4. Speedy analysis of these samples is important to minimise the effects of sample decay. The drawback with a trigger auto-sampler is that they do not capture the early part of an event when significant changes occur in the stream chemistry (c.f. Coalburn flow–solute relationships, Figure 3.7, and the initial pulse). The use of a rainfall trigger would resolve this issue. Furthermore, as mobile-phone technology improves it is possible to have telemetry for the stream and rainfall; when a storm is expected remote polling could be utilised activate the sampler.

The number of auto-sampler events required to calibrate the duration-frequency-magnitude is dependent upon the site risk and funds available. The Coalburn study revealed a marked difference between summer and winter events. As a minimum it would be sensible to sample one event during summer base-flow conditions (i.e. dry antecedent conditions) and one events during winter with wet antecedent conditions. Its is important to target the sampled events by using the flow record to ensure the full range of flow has been sampled and to capture behaviour such as the recovery at high flows observed at Coalburn.

The above appraisal is designed to capture the temporal variations in water quality, however, Coalburn has also demonstrated the importance of spatial variation in water quality within a catchment. The initial study included surveys to investigate the chemical and biological spatial variability and where spatial variability was identified, these surveys should be repeated under baseflow and highflow conditions for the chemistry and seasonally for biological sampling. This will allow the identification of spatial patterns in the catchment and the need to consider managing sub-catchments in different ways.

It is important the water quality sampling programme is in conjunction with biological assessment techniques as only with a combination of the two can the risk of acidification be fully assessed. For example, the Coalburn biological data indicates a taxa that is sensitive to acidification but not impoverished, whilst the water chemistry indicates pH and aluminium are beyond critical toxicity thresholds.

Measurement of the rainfall volume and chemistry are essential where the critical loads are exceeded, and would be recommended in most other situations. At Coalburn, the rainfall chemistry displays distinct marine and terrestrial signatures, although it was not possible to directly link these to chemistry in the stream. However, other catchments may be more sensitive to such signals (for example, thin soils on impermeable rock) and a knowledge of the acidic inputs is important as afforestation is likely to amplify these signals through scavenging, and this could affect the catchment acidity status. Routine chemical sampling and volumetric measurements of the rainfall and river also has the benefit of being able to derive gross catchment fluxes; indicative of the gross catchment processes.

The frequency of the rainfall sampling should again reflect the risks, however, for a gross assessment the twice monthly approach used at Coalburn would suffice. In general, the longer the sampling frequency the more smoothed the variation becomes. One fundamental issue that warrants some attention is ensuring that the rainfall will receive low level analysis and the limits of detection are suitably low.

Measurement of cloud mist and dry deposition component is difficult in terms of both collection and interpretation. However, these components are not necessary for a catchment appraisal; they can be inferred from the wet deposition signal and, from research catchments such as Coalburn, a precautionary principle applied. Furthermore, it should be remembered that the information may be available from sources such as the Meteorological Office and The Department of Environment, Transport and Regions.

Similarly, the measurement of throughfall and stemflow are not necessary for a catchment sensitivity appraisal. It would only be required to discuss the processes operating within a catchment.

Once the above data has been gathered the reporting and analysis stage requires consideration of all of the issues relating to management of acidification (Figure 7.2). These considerations should not just be in terms of the immediate consequence of the development but the whole life effect; furthermore the off-site effects such as downstream effects on bio-diversity also need to be considered.

The above appraisal strategies are aimed at new afforestation developments. However, the Environment Agency also needs to be mindful of and to assess the legacy of older/mature forests and their potential impact on the aquatic environment. Older forests will not have been subject to the same assessment or have benefited from the current land preparation and silvi-culture knowledge, techniques and machinery. Consequently, such forests may be located within sensitive catchments and have inappropriate artificial drainage networks that present a risk. The Environment Agency needs to identify these sites, assess if there is a current issue and whether factors such as nitrate excess, harvesting and restocking present a future risk. Where issues are identified, it may be necessary to invoke a monitoring programme (as per above), in close liaison with the Forest Authority/Commission to ensure forest management minimises the risks to the aquatic environment (for example moving from a single to a mixed age stand).

In summary, once a catchment is identified as sensitive (whether through a new or existing development) and requiring an appraisal to assess the risk of, the first step is to carry out an initial study. Where the initial assessment reveals a more intensive appraisal is required the components discussed above could be mixed and matched to achieve a suitable appraisal. Consultation and partnership with the relevant bodies would be an important element in deciding what a 'suitable appraisal' is, and ensuring the necessary information was gathered (i.e. cost-effective). The key steps of the catchment appraisal are summarised in Figure 7.3, while Table 7.3 estimates the costs of the appraisals.

While some may see such an approach as excessive in detail and cost (Table 7.3), legislation such as the Habitats Directive already require the relevant authorities to ensure ecologically favourable conditions are maintained for the protected species in river catchments designated cSAC's. Furthermore, developments in a cSAC requires an appropriate assessment to ensure favourable ecological conditions are maintained for the protected species. These assessments are likely to become more frequent in the future, particularity in Cumbria where stretches of the River Eden, River Derwent and River Ehen catchments have been designated cSAC's.

Table 7.3 Headwater appraisal strategies

Initial Study			
Item	**Days**	**Estimated cost (£ K)**	**Comments**
Desk study of catchment	3	0.45	
Biological assessment	6	0.90	
Chemical sampling	1	0.15	
Sample analysis	N/A	0.20	Assumed 10 samples, taken during winter period.
Catchment field assessment.	1	0.15	
Data analysis and reporting	5	0.75	
Initial Study Cost		2.60	
Intensive Study			
Item	**Days**	**Estimated cost (£ K)**	**Comments**
Flow monitoring equipment	N/A	2.50	Capital cost. Could be used in other assessments.
Auto-sampler	N/A	1.50	Capital cost. Could be used in other assessments.
Two raingauges for rainfall volumes and chemistry.	N/A	0.60	Capital cost. Could be used in other assessments.
Routine chemical sampling.	Inc below	0.96	Assumed twice a month for rainfall and stream – 48 samples in total.
Event sampling	Inc below	1.92	Four events with 48 samples per event – 96 samples in total.
Catchment chemical survey	Inc below	0.40	Assumed carried out twice for ten samples – 20 samples in total.
Biological sampling and analysis	3	0.45	One survey to compliment the initial survey.
Data collection	28	4.20	
Data validation	12	1.80	
Data analysis and reporting	20	3.00	
Intensive Study Cost		17.33	**Capital costs = £4.6K**

Assumed: Staff costs are £150 per day.

Samples costs are £20 per sample.

Intensive study runs for 12 months required to sample all the seasons

N/A – Not applicable

7.7 Summary

The discussion above confirms that the 'management of the catchment land-use needs to be considered as contributing to a sustainable management of the river catchment in the same way as hard engineering does' as stated by Newson (1996). The sites of primary concern are sensitive catchments where acidification could result from anthropogenic influences (e.g. nitrogen deposition or coniferous afforestation/forestry operations) and have a detrimental effect upon the aquatic ecosystem in the headwaters, with potential extensions downstream.

There is a need to constantly re-assess the approach to environmental management in an era of rapid change with new concepts and policies arriving in rapid succession. The science of forest hydrology and hydrochemistry is relatively new and moving at a pace, continually presenting new information for the policy makers. Consequently, the Environment Agency needs guidance from research literature and its own monitoring networks, such as the Coalburn study, about the extent and seriousness of present and future forestry impacts on the aquatic environment. The information gathered here would support the adoption of a precautionary principle where there is only partial understanding of a catchment. Such a partial understanding is partly inevitable, given that rapid spatial variability can occur in water quality. For example, at Coalburn, small differences in the glacial drift and the presence or absence of peat have a significant bearing upon the acidity of the runoff generated over distances of tens of metres.

During the research programme a duration, frequency and magnitude approach to acidification has successfully been adopted for Coalburn and has demonstrated that this could be applied on a less intensive scale for other catchments that are at risk of acidification. The discussion has also highlighted the fundamental issues surrounding the acidification issue and suggested that the Environment Agency could potentially use its LEAP documents to implement acidification management strategies for catchments.

In discussing the need to identify acid-sensitive catchments, particularly in terms of afforestation, the importance of carrying out chemical and biological monitoring was recognised. However, it is apparent that, within the Environment Agency, there is no national protocol for identifying the sensitive catchments, other than the critical load maps. These, on the evidence from Coalburn, may not be sensitive enough for catchment management. Furthermore, once a sensitive site is identified, the Environment Agency has no national method for carrying out site appraisals and translating water quality and biological information into a meaningful cause-effect-risk judgement (i.e. what is likely to happen if the development takes place and what are the risks of this prediction being wrong). The site appraisal should not only consider the current catchment status and the immediate impact of afforestation, but the range of potential impacts on the aquatic environment at all stages of the forestry cycle. Such protocols and assessments need to be developed within a national liaison structure between the Environment Agency and Forest Authority.

8 Coalburn: Summary and conclusions

8.1 Summary of research outputs

Since 1992, the Environment Agency has collected water quality data through regular sampling, event sampling and continuous monitoring, building an extensive database of high resolution data for the Coalburn catchment. Data has been collected through the later stages of forest canopy closure. This stage is likely to represents a period of distinct change in physical, hydrological and chemical terms, as the influence of forest crop starts to dominate over the drainage/moorland. This thesis offers a benchmark assessment of the Coalburn water quality that can be used by future studies to assess the changes in hydrochemistry as the forestry cycle progresses to felling and replanting (2011 and onwards).

Coalburn hydrochemistry has distinct chemical signatures and exhibits acid episodes; the causal mechanisms have been postulated in terms of fundamental hydrological and hydrochemical principles to produce the conceptual Coalburn runoff model. Mixing modelling was then applied to introduce a robust analysis into the process and the simplified Coalburn Model produced. Finally, the results were considered in terms of their wider relevance to environmental policy.

The overall aim of the Coalburn research programme is to 'determine in detail the hydrological effects of upland conifer afforestation' (Robinson et al., 1998). The objectives for this study relate to the water quality aspects, at a catchment scale, of this hydrological assessment and ten objectives were set out in Chapter 1; these are considered and summarised with respect to the preceding chapters:

Objectives 1 & 2: ***Assess the episodic acidification status of the Coalburn catchment. If the acidification is episodic then determine the magnitude, duration and frequency of the acid events.***

There were three distinct sources of acidity identified in the Coalburn catchment that can be classified into:

- Organic and humic acids derived from the peat and pine needle litter layer under the forest.
- Mineral acids derived from wet, cloud mist and inferred dry deposition of non-marine sulphate, nitrate and ammonium.
- The rainfall, cloud mist and inferred dry deposition exhibit periods of increased sea-salt deposition that could be the precursor of a sea-salt acid event (although not observed in this study).

While each of the above are distinct sources, it is not possible to apportion the acidity observed in the Coalburn stream directly to each source; catchment processes integrate them into a single response. However, the catchment hydrochemistry indicates the acidity is primarily derived from the peat soils within the catchment.

The cloud mist and precipitation at Coalburn are slightly acidic and the catchment can receive moderate levels of acid deposition through the wet and dry deposition pathways, particularly when the winds have tracked from an easterly direction.

At the outfall, Coalburn streamwater chemistry was acidic and is a transitional site as defined by Ferrier and Harriman (1990). Coalburn streamwater chemistry exhibits consistent patterns in the base- and storm-flow chemistries; base-flow chemistry being well buffered and storm-flow displaying acidic episodes. The duration-frequency-magnitude of the Coalburn acid

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At the outfall, Coalburn streamwater chemistry was acidic and is a transitional site as defined by Ferrier and Harriman (1990). Coalburn streamwater chemistry exhibits consistent pattern in the base- and storm-flow chemistries; base-flow chemistry being well buffered and storm flow displaying acidic episodes. The duration-frequency magnitude of the Coalburn acid episodes revealed them as being less frequent than expected but with a longer duration. The acid events exceeded environment quality standards: pH and aluminium concentrations would suggest the acid events are toxic. However, the elevated calcium concentrations and presence of humic substances reduces the biological impact.

The acid events were classified into those with dry antecedent conditions (DAC) and those with wet antecedent conditions (WAC). The WAC event were more frequent in winter, more acidic and had a longer duration in comparison to the DAC events that were more frequent in the summer. This has implications for the biological impact of acid events; during the winter month the invertebrates can take shelter in the hyporheic zone and are less likely to be impacted by the acid events. In contrast, during the summer months, when the invertebrates are more active, the acid events are less severe.

The analysis has highlighted the fact that duration-frequency-magnitude are intrinsically linked. To assess the impact of acid events on a stream the duration-frequency-magnitude need to be considered in terms of the chemical and biological indicators. Without this holistic approach, incorrect conclusions and management decisions will be made.

Objectives 3,4 & 5: Identify the important chemical signatures in the Coalburn catchment.

The important chemical signatures have been identified for the Coalburn catchment in terms of:

• Solute signatures	(Table 8.1).
• Hydrological component signatures	(Table 8.2).
• Flow variation signatures	(Table 8.3).
• Event signatures	(Table 8.4)

The identification of these hydrochemical signatures and linkages to sources, pathways and relative mixing of these components has been fundamental in hypothesising the causal mechanism behind the Coalburn catchment response. In using the chemical signatures to postulate the causal mechanisms there has been consistency, which serves to reinforce the validity of the hypotheses/observations.

The gross catchment fluxes were estimated and these demonstrate the solute flux signatures can be separated into two groups. The first group includes those derived primarily from the dry deposition and/or catchment source and include aluminium, calcium, sulphate, dissolved organic carbon, total organic carbon and iron. The second group are those derived primarily in the rainfall and appear to be retained in the catchment and include magnesium, sodium, potassium, nitrate and ammonia.

The method of identifying chemical signatures for the elements of the hydrological cycle and hypothesising the flowpaths and mechanisms is not new. However, few catchments are studied at the requisite intensity and longevity required in undertaking such an analysis. The analysis of Coalburn data in this manner has only been possible through a combination of the long-term catchment monitoring and short-term process studies. Nevertheless, the Coalburn data makes a contribution to the overall scientific knowledge of these signatures in UK catchments and specifically to those in upland Northern England.

Table 8.1 Solute characteristics in the Coalburn catchment

Solutes	Source	Comments
pH Alkalinity	Catchment	The pH and alkalinity strongly replicates the gradients in the catchment soils and the source of the water (i.e. soil or deep-water). pH is an indicator of the source of water in the catchment.
Chloride	Atmospheric (Marine)	Atmospheric tracer due to its conservative behaviour.
Sodium	Atmospheric (Marine)	Not a good source indicator.
Sulphate – non marine.	Atmospheric (Terrestrial)	Winds from an easterly direction yields precipitation, cloud mist and inferred dry deposition with elevated concentrations of sulphate. The link between deposition and stream acidification is complex and mediated by catchment processes.
Nutrients ammonium nitrate	Mainly atmospheric (Terrestrial)	Nutrients observed in high concentrations in the rainfall and cloud mist, however, are rarely present in the streamwater in similar concentrations.
Calcium and magnesium	Catchment (Deepwater/ peaty-gley)	These solutes are indicative a catchment pathway/sources, specifically water that originated from the deepwater pathway.
DOC, TOC and Colour	Catchment (Peat/soil water)	These solutes have temperature induced seasonal trends, but can be used as a source indicator of peat waters.
Aluminium	Catchment	Elevated aluminium concentrations are indicative of soil water.
Manganese	Catchment	Elevated manganese concentrations are indicative of soil water.
Iron	Catchment	Indicative of catchment sources.

Table 8.2 Hydrological component signatures in the Coalburn catchment.

Signature	Characteristic
Throughfall (Hind, 1992; Wake, 1994)	Compared to incident rainfall the throughfall generally has lower pH, higher conductivity and concentrations of Ca, Mg, Na and K.
Stemflow (Hind, 1992; Wake, 1994)	Compared to incident rainfall and throughfall generally has lower pH, higher conductivity and concentrations of Ca, Mg, Na and K. The stemflow chemistry is different for trees growing on the different soils: Mn and K concentrations are believed to be greater on the peaty-gley soils, while the stemflow is more acidic on the peat soils.
Base-flow	High pH; high conductivity; base cations rich and positive alkalinity
High-flow	Low pH; lower conductivity; base cation depleted and decreases colour; increased aluminium and negative alkalinity
Peat-soil	Low pH; low conductivity; base cations depleted; elevated aluminium; elevated TOC/DOC; coloration and negative alkalinity
Peaty-gley	High pH; high conductivity; elevated base cations; little coloration and positive alkalinity.

Table 8.3 Flow variation signatures in the Coalburn catchment

Phase	pH Flowpaths & causal mechanisms	Conductivity Flowpaths & causal mechanisms
1. Base-flow-Rapid decline	Under low flow conditions the stream chemistry is dominated deep-water, and while the flow may decrease there is no major change in the flowpath or the chemistry. During the early part of an event the flow increases and there is a rapid decline in pH as the deep-water is diluted by soil and peat sub-catchment water.	During base-flow the conductivity increases as the deepwater (and upwelled peat water) dominates, reflecting its association with long residence times in or near to the boulder clay and elevated concentrations of weathered products. However, during an event this is rapidly diluted by soil and peat sub-catchment water.
2. Transition.	As flows continue to increase a more complex mixing process occurs; the relative contributions from the different upper and lower soil horizons gradually change as the catchment wets up. In the transition zone demonstrates pH decreases as flow increases as flowpaths switch to acidic horizons and catchment areas that make up an increasing component of the stream chemistry. The transition zone represents the most difficult catchment response to explain, with broad variation in pH for a flow reflecting: antecedent catchment conditions; event characteristics; flowpath and residence time.	As flow rises an increasing component is derived from the more acidic soil and peat sub-catchment waters and the hydrogen, aluminium and organic ions concentrations increase and this results in an increase in conductivity.
3. Stable low.	At high flows the catchment stabilises. As flow continues to increase the pH begins to stabilise, i.e. the catchment has established either preferred water pathways, which contribute a water of constant chemistry; or efficient mixing of the water from various sources produces a constant chemistry.	At a threshold either a washout process occurs or an event water signal reaches the stream and a transient dilution response occurs.
4. Recovery	During extreme hydrological events there would appear to be a recovery in the pH suggesting that event-water may be reaching the main channel through infiltration/saturation excess (reflecting the saturated catchment conditions) or a 'washout' process is occuring.	No Phase 4 was observed for conductivity at Coalburn

Table 8.4 Event signatures in the Coalburn catchment

	Antecedent Wetness	Pollution Climatology	Event Conditions
pH Response	Wet antecedent conditions are signified by an initial pulse. The same pulse is not evident with dry antecedent conditions.	Catchment processes dominate the pH response. There was no evidence of linkage between rainfall and stream pH. Even during extreme rainfall events rapid modification of rainfall pH generally occurs.	Catchment gradients and processes dominate. Even during extreme events, there is only a slight recovery. The intensity and magnitude of an event is positively correlated with the rates of change and severity of the acid episode.
Conductivity Response	Wet antecedent conditions are signified by an initial conductivity fall, which is not evident with dry antecedent conditions.	There is evidence that when distinct rainfall signatures impact on the catchment they can be observed in stream chemistry. This implies the pollution climatology can affect conductivity during and following an event. However, this does not over-ride the catchment gradients or occur for less extreme events.	Catchment gradients and processes dominate. However, during extreme events the rainfall signal may reach the stream and result in a recovery. The intensity and magnitude of an event is positively correlated with the rates of change and severity of the conductivity response.

Objective 6: Ascertain if a link can be established between the deposition and stream chemistries.

Wind direction and duration of flow from that direction have a bearing upon the input of ions from the atmosphere at Coalburn. Winds from the easterly sector carried a 'terrestrial' chemical signature that was more acidic and had higher concentrations of acid anions. The westerly 'marine' winds had a signature of high pH and elevated concentration of marine ions.

At Coalburn, it was possible to demonstrate the rainfall chemistry signal can modify the stream chemistry (with respect to chloride and conductivity). The response was not a direct one and could only be observed following extreme deposition events (which were few given the sampling frequency smoothing effect). The time lag implies the rainfall chemistry has a role in modifying the catchment stores and the subsequent event's stream chemistry; the effects of an input signal becoming progressively more dilute. During extreme high flows, there was evidence that the rainfall signal may have a direct influence on the stream chemistry. This implies the antecedent conditions (i.e. quality of the pre-event water); residence time of that water (i.e. time for modification) and event conditions are important in controlling the catchment's response.

Objective 7: Apply hydrological principles and chemical signatures to conceptualise the likely causal mechanisms underlying the acid events at Coalburn.

Overall, the hydrochemical response and episodic nature of the acidification reflects the catchment structure, soil type, underlying geology and the chemical gradients. Variation in the water quality would appear to be accounted for by: the physical attributes of the catchment: antecedent and event conditions; hydrological pathways and residence times. Essentially, varying proportions of chemically different waters from these sources can be used to explain the observed catchment response at any one time. Superimposed onto this are the temporal variations that are driven by climate and biological mediation.

The Coalburn catchment has distinct vertical chemical gradients that are typical for British upland catchments with a substrate of high buffering capacity and organic rich peat surface horizons. In addition, the soil distribution introduces a component of spatial variability into the water chemistry at Coalburn. Two chemical signatures from the peat and peaty-gley sub-catchments were identified and the distribution and dynamic lateral variability influenced the streamwater hydrochemistry observed at the catchment outfall. Thus, at Coalburn the catchment's hydrochemical response needs to be though of in terms of varying proportions from a vertical and lateral component that have distinct signatures.

The regular hydrochemical response at Coalburn was linked to the flowpath(s) and residence times that result in varying proportions of event and pre-event water from the lateral and vertical hydrological pathway(s). However, the 'regular' response was modified by the antecedent wetness, pollution climatology and event characteristics; the Coalburn events could be classified according to these parameters (see Objective 8 below).

By ascribing a chemical signature to components of the hydrological cycle the broad processes underlying the Coalburn catchments hydrochemical response can be explained. Previous process studies (short-term and relatively inexpensive) at Coalburn have given valuable information supporting this analysis. However, there is uncertainty in back-casting the hydrochemical processes from the catchment scale response alone, considering the temporal and spatial variations that have been encountered in the Coalburn catchment.

The patterns observed in the linkage between the rainfall and stream conductivity reveal/infer some important characteristics of the processes operating in the Coalburn catchment. For small/medium rainfall events, the catchment response is dominated by pre-event water and the Coalburn hydrochemical response can largely be explained by the chemical signatures observed within the catchment. However, when the catchment is saturated the rainfall signal can reach the stream and an element of event water contributes to the hydrochemical signal (reflected in the recovery of the pH and conductivity at extreme flows). These results are consistent with the observations of Robson (1993): the stream hydrochemical response to rainfall is better viewed as a function of the mix between the various stores of water in the catchment and in terms of residence times.

The distinct vertical and lateral chemical gradients and signatures have been used to explain the hydrochemical response at Coalburn in terms of varying proportions of water from each of these catchment sources. While the chemical signatures are important, it should be remembered that improved artificial drainage has an important role in rapidly delivering these signatures to the main channel, with little residence time for buffering. Indeed the drainage still exercises considerable influence upon the catchment hydrochemical response after 27 years. This is highlighted by the pH and conductivity pulse observed prior to some events at Coalburn, which has been linked to improved drainage.

In summary, the catchment response at the canopy closure stage of growth is a complex integration of: antecedent conditioning; catchment inputs; canopy soil and drainage effects and event/pre-event water. The balance between these factors is critical to the hydrochemical response and changes in these will be the focus of future studies.

Objective 8: Derive a classification system for the acid episodes observed at Coalburn based on the catchment scale response, characteristics and signatures.

A classification system was derived for the acid episodes observed at Coalburn according to the antecedent wetness and event conditions (rainfall volume and intensity), with events being observed for all the categories except dry antecedent conditions with snow which are rare at Coalburn (Table 8.5). The original classification system included the antecedent pollution climatology to reflect the potential importance of catchment conditioning. However, the data gathered is not of sufficient resolution (particularly the rainfall sampling) to fully assess the differences between acid episodes where the catchment has been conditioned by the terrestrial and marine signatures, and further work is required.

As with all classification systems, it can never capture the infinite variability of the catchment response, however, at a generic level the system appeared to work well.

Table 8.5 Coalburn acid event classification

	Event Conditions		
Antecedent Conditions	Normal	Intense	Snow or Snow Melt
Wet	✓	✓	✓
Dry	✓	✓	✗

<u>Key</u>

✓ = Event observed at Coalburn.

✗ = Event not observed at Coalburn during this study.

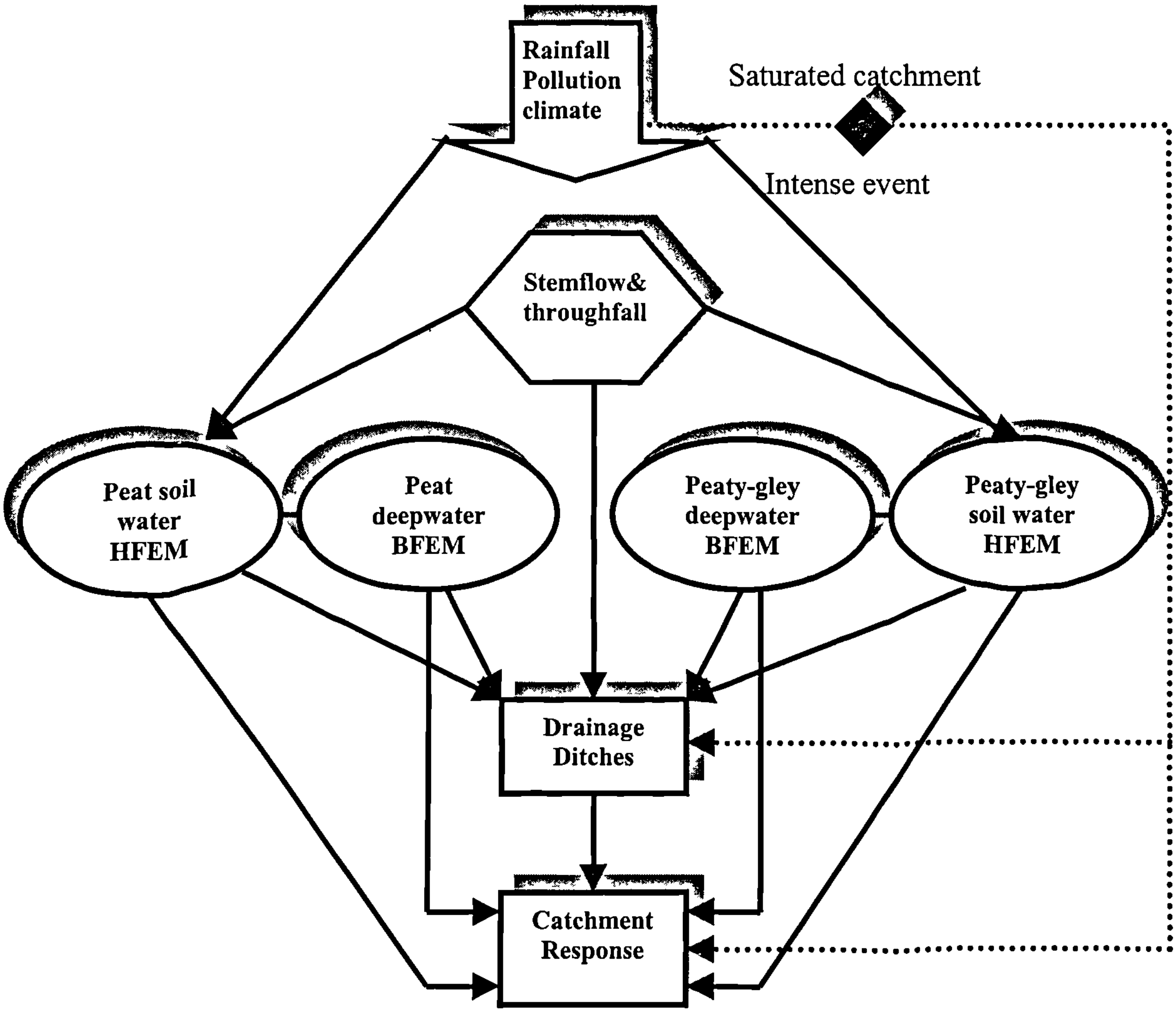
Objective 9: Apply mixing modelling techniques to the Coalburn data and derive a conceptual Coalburn model of the Coalburn hydrochemical response.

Initially, a basic Coalburn runoff model (based on the Birkenes model) was produced to facilitate the conceptualisation of the flowpaths and processes causing the catchments hydrochemical response. To introduce a robust analysis to this process mixing modelling was successfully applied to the Coalburn data and this has produced valuable information on the flowpaths and residence times in the Coalburn catchment. However, this must be tempered against the uncertainties inherent in the derivation of the ANC and endmember values. Care was also required in interpreting the end-members in terms of the vertical and lateral pathways.

Application of the mixing model revealed the Coalburn hydrochemical response can broadly be explained by catchment processes and varying contributions from the base and high-flow endmembers; however, during extreme hydrological events a third endmember was required. This suggests that, under most conditions, the rainfall displaces pre-event water bearing the chemical fingerprint of the catchment endmembers, while during extreme events a component of event water is introduced. These results should be tempered by the fact the actual flowpaths and sources within the catchment are still unknown.

The mixing model exhibits distinct differences between events with dry and wet antecedent conditions demonstrating the event starting point is fundamental in determining the catchment hydrochemical response and processes operating. The initial pulse observed during wet antecedent events was explained by the mixing model as a function of a rapid delivery of deep-water from near the channel and/or from the peaty-gley sub-catchment. The initial pulse occurs in all events, however, the pH and conductivity response was only observed during wet antecedent conditions. There was evidence that other solutes, such as colour, may exhibit a similar pattern.

Figure 8.1 The Coalburn model



Key

·············· 3rd endmember

BFEM Baseflow endmember.

HFEM Highflow endmember.

At Coalburn, the base-flow endmember has an important ameliorative role in reducing the event duration, magnitude and toxicity; any changes in management that would exclude or reduce this component would have a detrimental impact on the Coalburn hydrochemistry.

A conceptual model of the Coalburn hydrochemical response was produced and it would appear to provide a reasonable framework to predict the hydrochemical response at Coalburn (Figure 8.1).

Objective 10: Appraise the relevance of the information presented as part of this research programme to public policy and the Environment Agency operations.

There is a need to constantly re-assess the approach to environmental management in an era of rapid change with new concepts and policies arriving in rapid succession. Furthermore, the science of forest hydrology and hydrochemistry is moving at a pace and is continually presenting new information to environment managers and policy makers. Consequently, the Environment Agency needs guidance from research literature and its own monitoring networks, such as the Coalburn study, about the extent and seriousness of present and future forestry impacts on the aquatic environment. The studies reported here have contributed to the understanding and calibration of the temporal and spatial variability (and hence risk) observed in the processes operating in upland catchments, such as Coalburn. In doing so it has highlighted the need to adopt a precautionary approach where there is only partial understanding of a catchment; given that rapid spatial variability can occur in water quality observed at Coalburn.

A duration-frequency-magnitude approach to acidification has successfully been adopted for Coalburn and has demonstrated that this could be applied on a less intensive scale for other catchments that are at risk of acidification. The discussion has also highlighted the fundamental issues surrounding the acidification issue and has suggested that the Environment Agency could potentially use its LEAP process to implement acidification management strategies for catchments (Newson, 1996).

In discussing the need to identify acid sensitive catchments, particularly in terms of afforestation, the importance of carrying out chemical and biological monitoring was recognised. However, it is apparent that there is no national protocol of identifying the sensitive catchments other than the critical load maps. These, on the evidence of Coalburn, may not be sensitive enough for catchment management. Furthermore, once a sensitive site is identified, the Environment Agency has no national methodology for translating water quality and biological information into a meaningful risk assessment. The site appraisal should not only consider the current catchment status and the immediate impact of afforestation, but the range of potential impacts on the aquatic environment at all stages of the forestry cycle. Such protocols and site appraisals need to be developed within a national liaison structure between the Environment Agency and Forest Authority/Commission.

8.2 Discussion

8.2.1 Coalburn: its contribution to science and policy

Research into the hydrological and hydrochemical effects of upland afforestation has typically focused upon initial land preparation, mature plantations or harvesting operations, leaving a hiatus in the understanding of the forestry cycle. The Coalburn study offers the opportunity to bridge this gap and is unique in Britain, being a long-term experiment aiming to provide detailed hydrological records of the impacts of afforestation throughout the forestry cycle. The Coalburn catchment was established in 1966 and data has been gathered for five years prior to afforestation and the first 27 years of forest growth.

The Coalburn and other similar studies of acidification have consistently demonstrated the importance of spatial variability in the local geology, soils, tree species etc. The water quality element of the Coalburn research programme has contributed to the scientific knowledge by:

- Identifying the key chemical signatures and variations in solutes at Coalburn.

- Identifying the duration-frequency-magnitude and toxicity of acid events at Coalburn and the processes by which they operate.

- Hypothesising the hydrochemical processes operating at Coalburn to produce the conceptualised Coalburn Model. This has highlighted the extent of lateral and vertical variability in hydrochemistry with in a small catchment and indeed over a distance of tens of metres.

- Discussing the role of pre-event and event-water and the influence of pollution climatology which extends the management of acidification issues at Coalburn, and similar catchments, beyond the catchment to the international scale.

- The study has extended the knowledge of the likely effects of coniferous plantation afforestation. In knowing the likely processes, the effects, risks and benefit of new plantation's or existing forestry can be assessed and the precautionary principle applied accordingly.

- A basic policy framework and protocols for catchment assessments were suggested to manage the acidification issues within a catchment.

Such information is essential to calibrate the temporal and spatial variability and hence risk; allowing policy makers and environment managers to make informed decisions.

The Coalburn research programme has also highlighted the temporal variations in the effects of coniferous afforestation in headwater catchment throughout the cropping cycle (e.g. the effectiveness of drainage ditches). Consequently, there is a need to maintain the funding of long-term research programmes, such as Coalburn, to provide long-term data that can be used to validate short-term low cost studies (McCulloch, 1997).

The benefit of collecting continuous pH and conductivity data at Coalburn has been clearly apparent in this study. The data provide a clear picture of the acid episodes in the Coalburn chemistry and allowed a more detailed analysis of the short-term catchment scale dynamics; considering the duration-frequency-magnitude of the events. Given data of reasonable accuracy, it is an improvement over deriving extreme values from applying statistical techniques to a limited number of spot samples; it effectively removes the dilemma of what is an appropriate technique (Robson, 1993). The down side to the collection of continuous pH and conductivity data is the infrastructure, maintenance and analysis time that is required to ensure data of reasonable accuracy. All of these have a cost, which were estimated as £150K capital cost and annual operational cost of £15.24K for the Environment Agency contribution to the Coalburn collaborative research programme. These costs must be offset against the benefits discussed above. Furthermore, the collection of continuous data may have other benefits for the Environment Agency such as 'real-time' pollution monitoring and reduction in the need for operational sampling.

8.2.2 Further work: Coalburn

The catchment response at the canopy closure stage of growth is a complex integration of the antecedent conditioning, catchment inputs, canopy, soil and drainage effects. The balance between these controls is critical to the hydrochemical response and changes in these will be the focus of future studies. In addition to this 'general' aim of future studies a number of specific areas that would benefit from future work were identified:

- The current sampling frequency has a tendency to smooth the extreme variations in the rainfall and cloud mist chemistry. To assess the hypothesised link between the catchment inputs (including pollution climatology) and the steam, an intensive period of rainfall, cloudmist and river chemistry monitoring would be required.

- To elucidate on the causal mechanism of the initial pH and conductivity pulse it would be beneficial to implement an intensive sampling programme on the main stream and tributaries near the catchment outfall during the early phases of an event. The chemical analysis should be for the full suite of determinands (Table 2.4) to identify if the initial pulse occurs in other solutes (e.g. colour). It may also be useful to carry out volumetric measurements at the same time.

- The pattern in iron concentrations was complex and further investigation into the sources of iron was required, particularly at low flow. This could be undertaken as a short-term intensive spatial sampling exercise.

- While the conductivity measurement has been problematic, it has provided valuable data. There was evidence that conductivity data could be utilised further, particularly in estimating the effects of pollution climatology and residence time. To fully utilise the conductivity for this improved field equipment would be required so that accurate continuous conductivity monitoring of both the rainfall and catchment outfall could be carried out at a suitable frequency.

- Identification of other endmembers would facilitate further mixing modelling, and perhaps a better understanding of the processes operating. The groundwater endmember was estimated from the stream chemistry, however, the presence of dipwells and piezometers imply the groundwater could be sampled directly to estimate this value. A third endmembers was required in the mixing model and this remains unidentified. The use of other chemical signatures such as DOC and luminecence to identify other endmembers should be investigated to resolve the difficulty of teasing the lateral and vertical signatures apart.

- The pH and conductivity probes (along with the auto-sampler) should be relocated to the natural channel upstream of the weir pool due to issues such as the location error that have been observed in this study.
- The upwelling of deeper mineral rich waters was hypothesised as a causal mechanism for the higher pH values observed on some of the 'peat' sites during low flow conditions. Some focused sampling and field surveys are required to fully assess this hypothesis.

8.2.3 Future issues: general

The study of acidification processes in afforested catchments is still a relatively new science and while the Coalburn research programme has contributed to this knowledge there is a need to continue long-term experiments, such as Coalburn, to elucidate on more general topics:

- How does the development of the forest canopy affect the input flux as the crop continues to grow?
- How long will the effects of the land preparation and drainage last?
- When or will the Coalburn catchment reach nitrogen excess and what effect will this have on the acidity status of the catchment?
- How will changes in the climate and/or pollution climatology affect the catchment response?
- Will there be deterioration in the water quality and bio-diversity in the River Irthing downstream as the forest develops?
- How does the acid deposition affect catchments such as Coalburn where organic acidity is dominant and how will external factors (e.g. climate change) affect this?
- There is a need to improve continuous monitoring probes as even something as simple to measure as conductivity can be problematic when measured in the field.

8.3 Concluding remarks

In studying the Coalburn hydrochemical response, it is apparent that the nature and extent of the temporal and spatial variability at Coalburn is infinite. As scientists and researchers, it is not possible to describe processes and model catchments to fully incorporate or predict this variability, and a compromise between the practicalities and cost of research have to be found.

The Coalburn research programme approached this issue by continuously monitoring the catchment scale pH and conductivity response; allowing a detailed duration-frequency-magnitude analysis of the catchment response (for pH and conductivity), with other solutes measured on a less frequent basis. It was then necessary to simplify the variation by identifying the key hydrochemical patterns and signatures in order to model or describe the processes operating. However, in simplifying the response assumptions are introduced (e.g. giving a hydrological component a chemical signature). Thus, in presenting a model of processes that underpin a catchment's hydrochemical response these assumptions should be remembered. However, the measurement of continuous data, at Coalburn, allows the calibration of the assumptions, errors and risks giving an indication of the degree to which the precautionary principle needs to be applied by the environmental managers or policy makers.

The use of a combination of continuous and sampled data provides another research framework to investigate some of the remaining water quality issues. Furthermore, the approach has relevance to operational monitoring for the Environment Agency; for example, real-time monitoring at key points to supplement the sampling network could give a better indication of the true variation in water quality.

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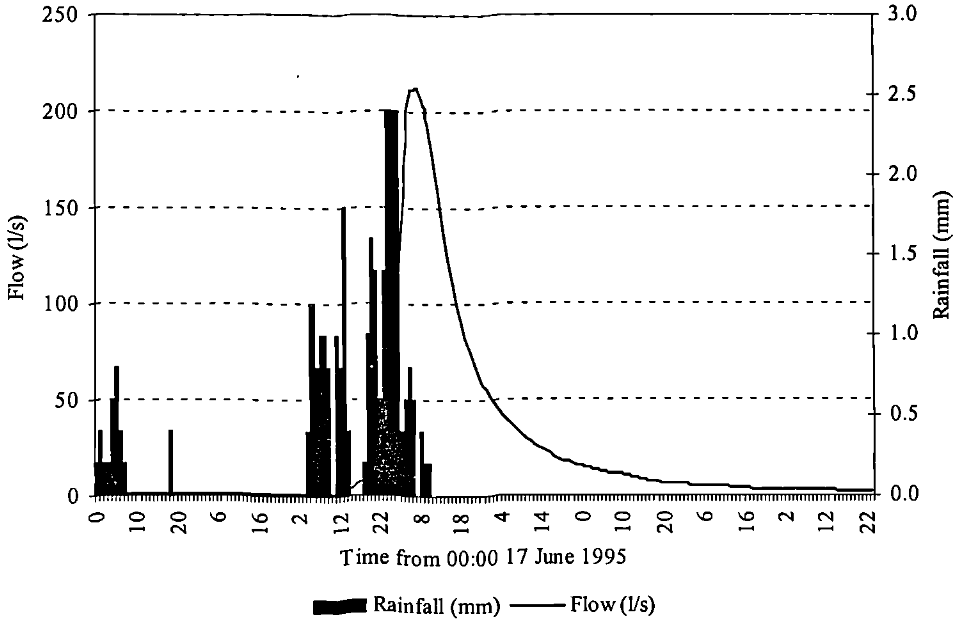
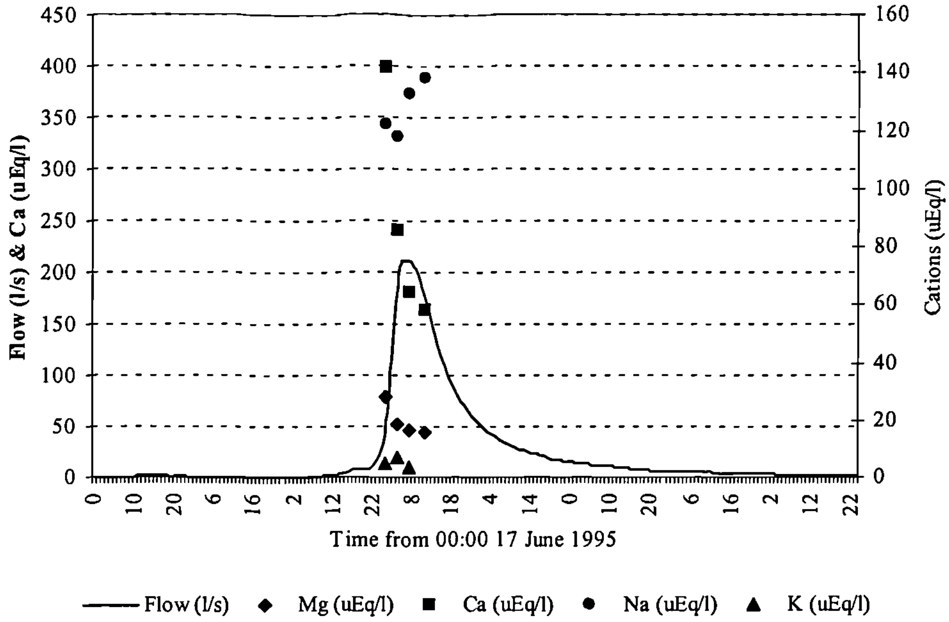
Appendices

Appendix A Event 1 19 June 1995

Appendix A1 Coalburn Event 1 19 June 1995 flow and rain time series



Appendix A2 Coalburn Event 1 19 June 1995 flow and cation concentration time series



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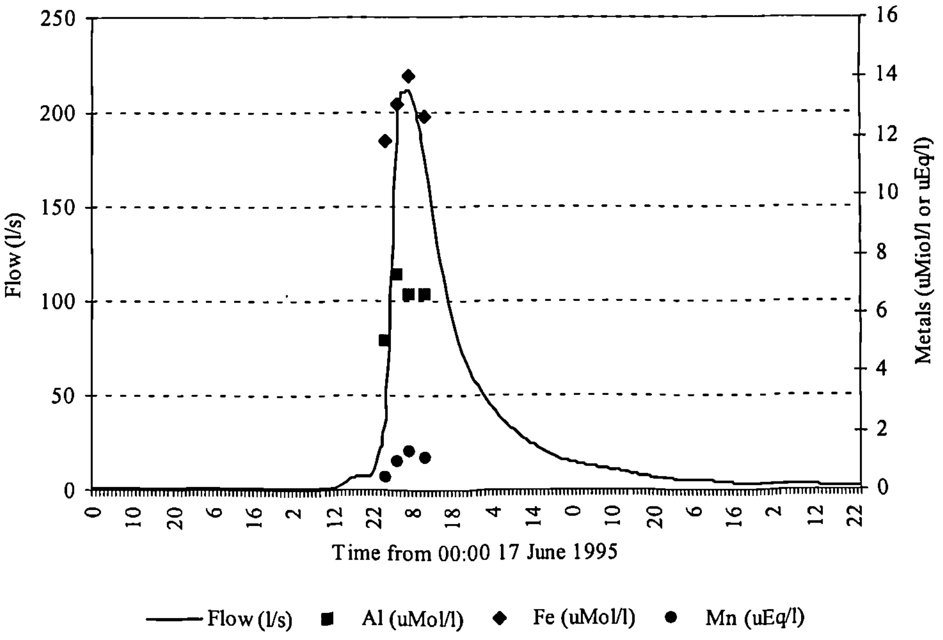

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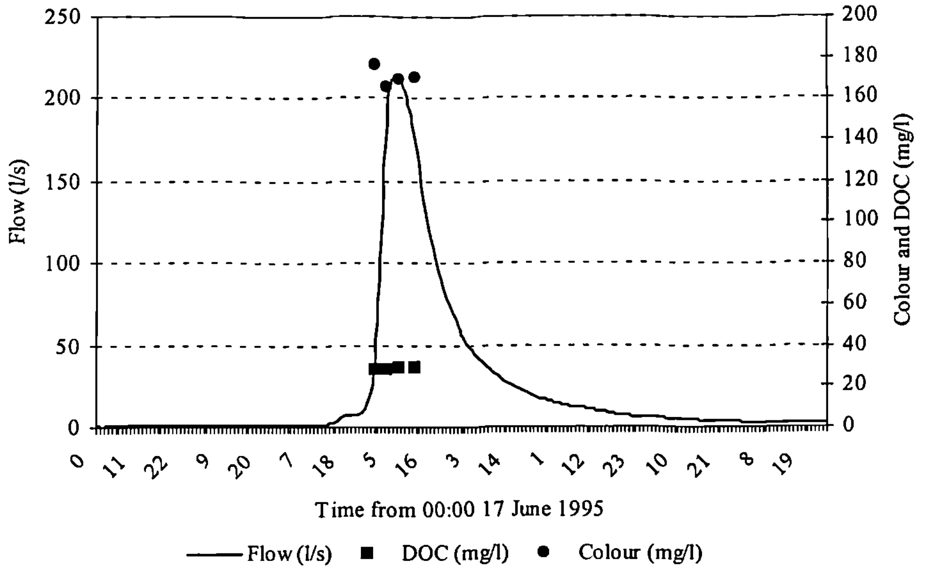

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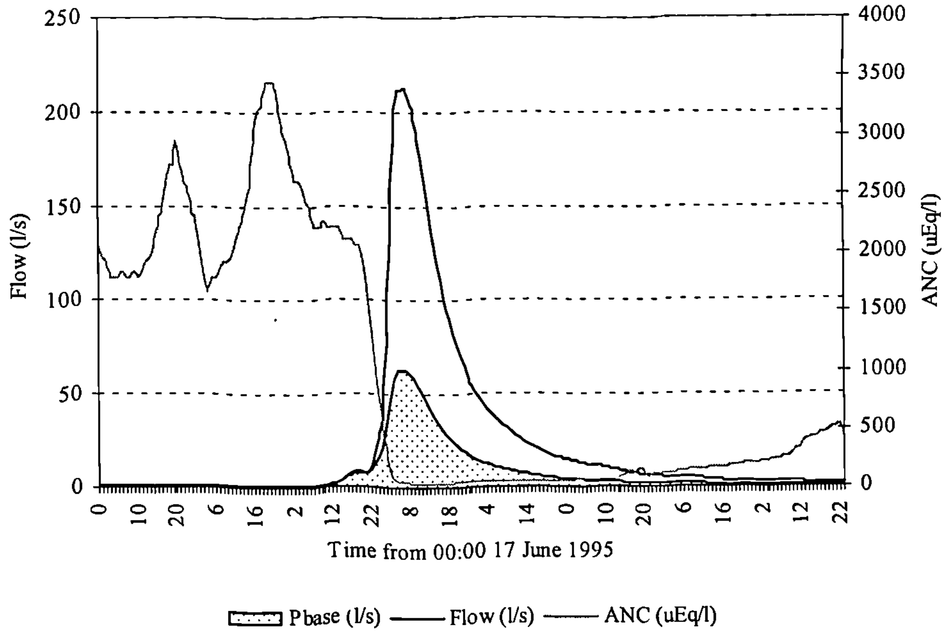
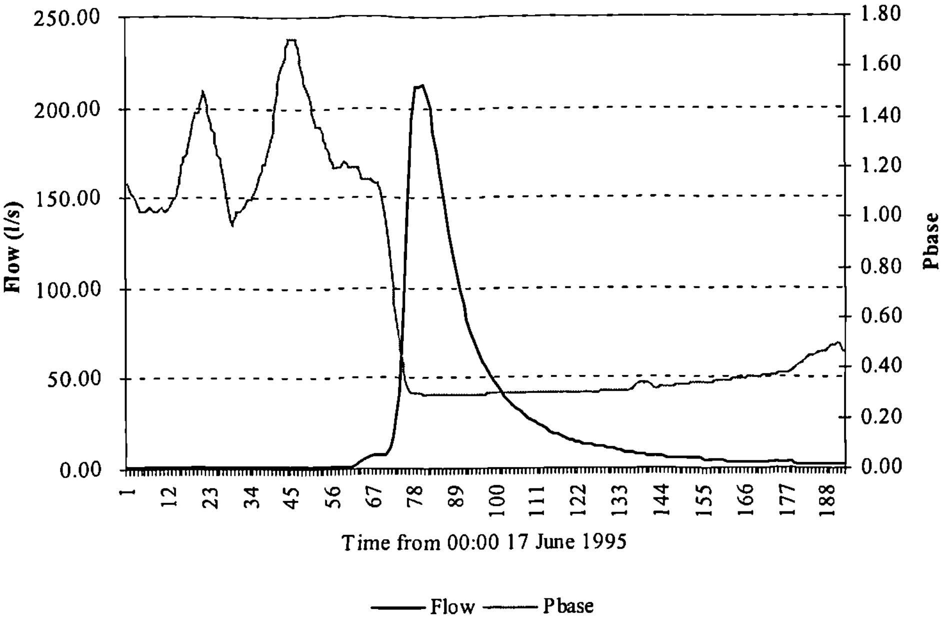
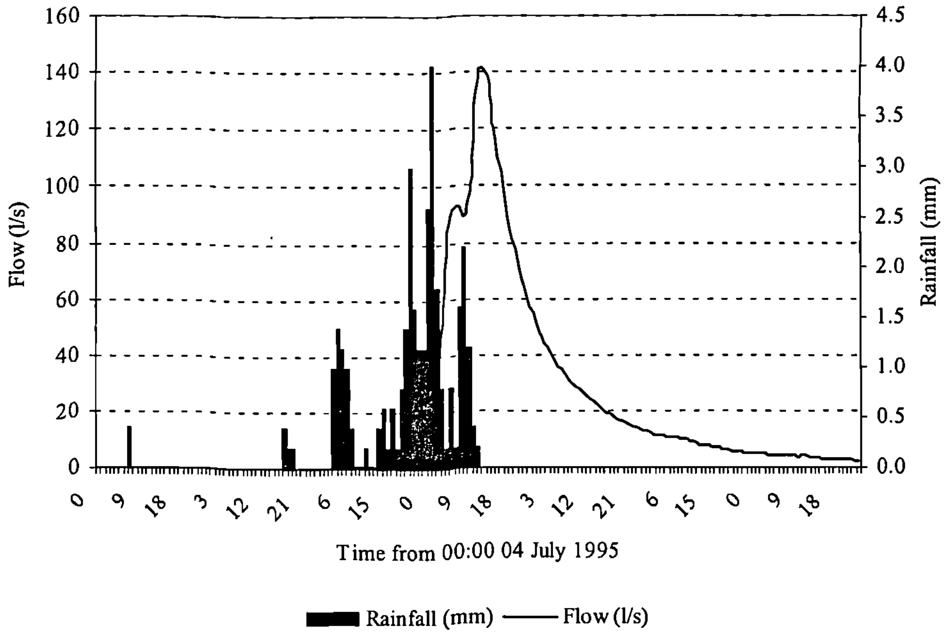


Appendix A6 Coalburn Event 1 19 June 1995 flow and P_{base} time series



Appendix B Event 2 06 July 1995

Appendix B1 Coalburn event 2 06 July 1995 flow and rain time series



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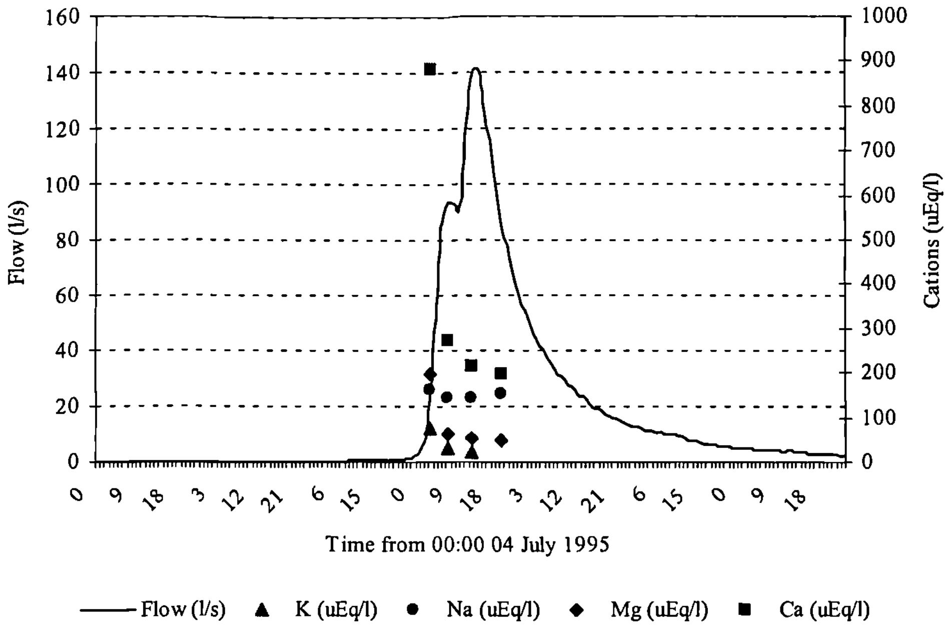

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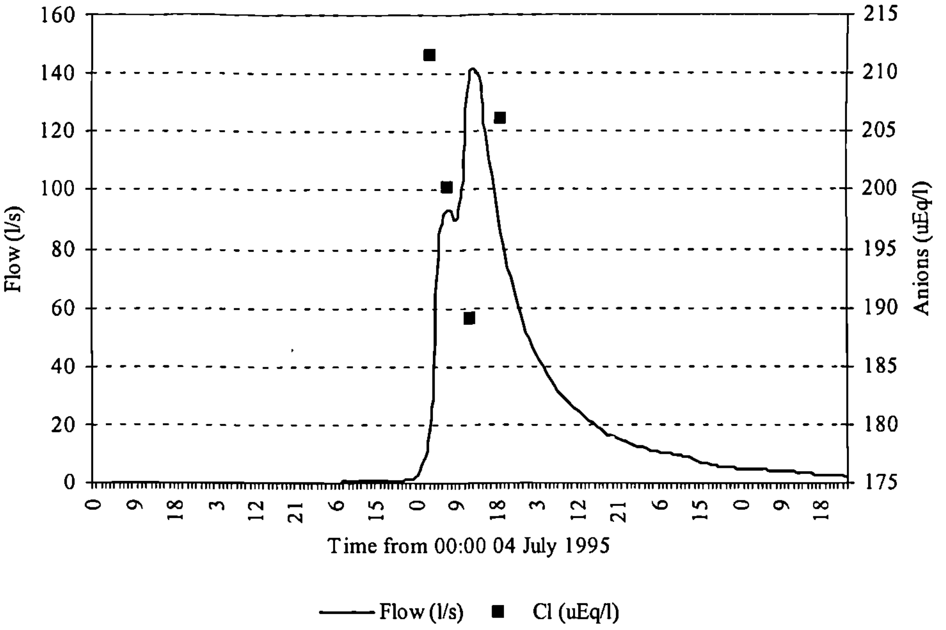

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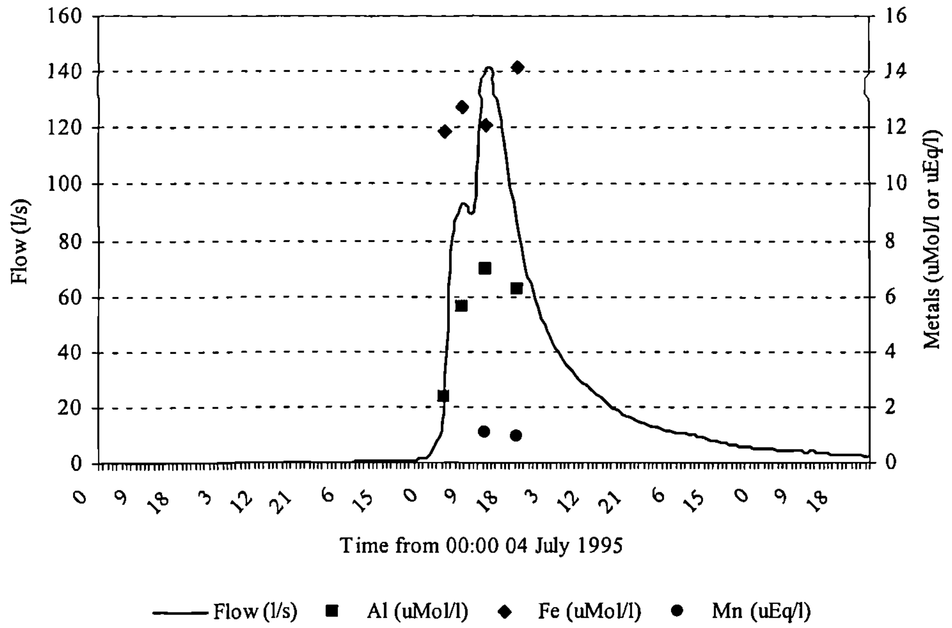
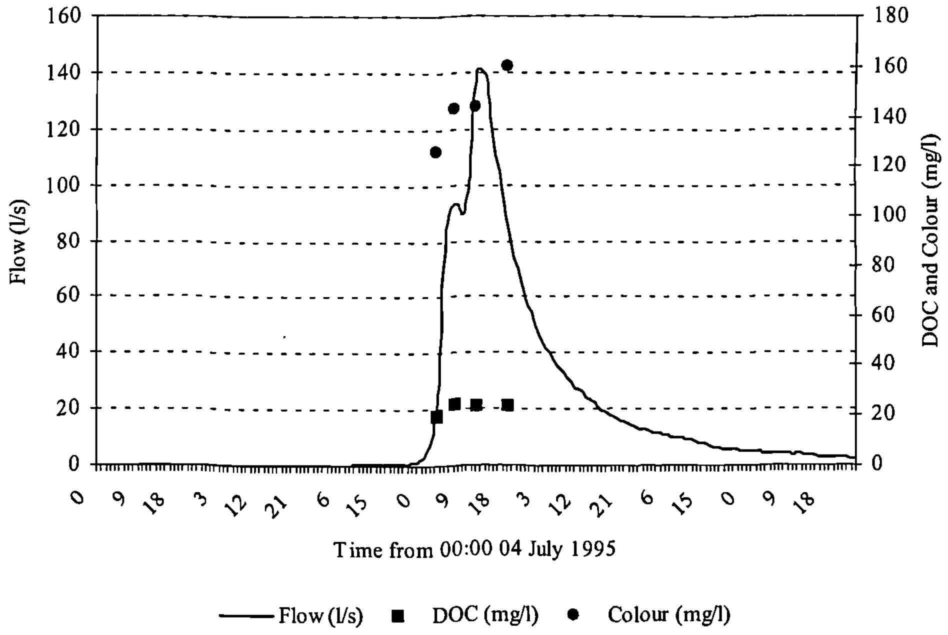


Appendix B5 Coalburn event 2 06 July 1995 flow, colour and DOC time series



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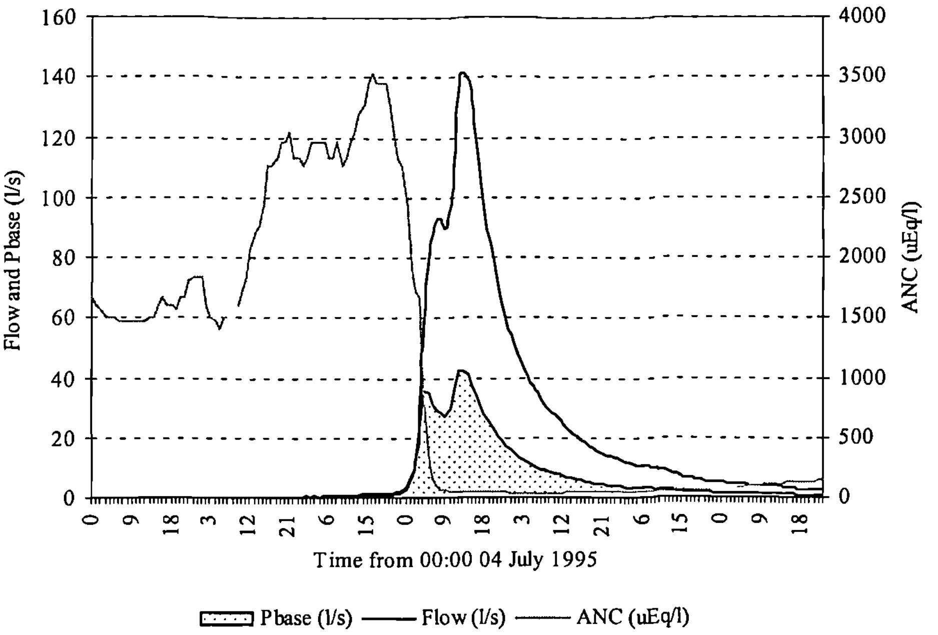
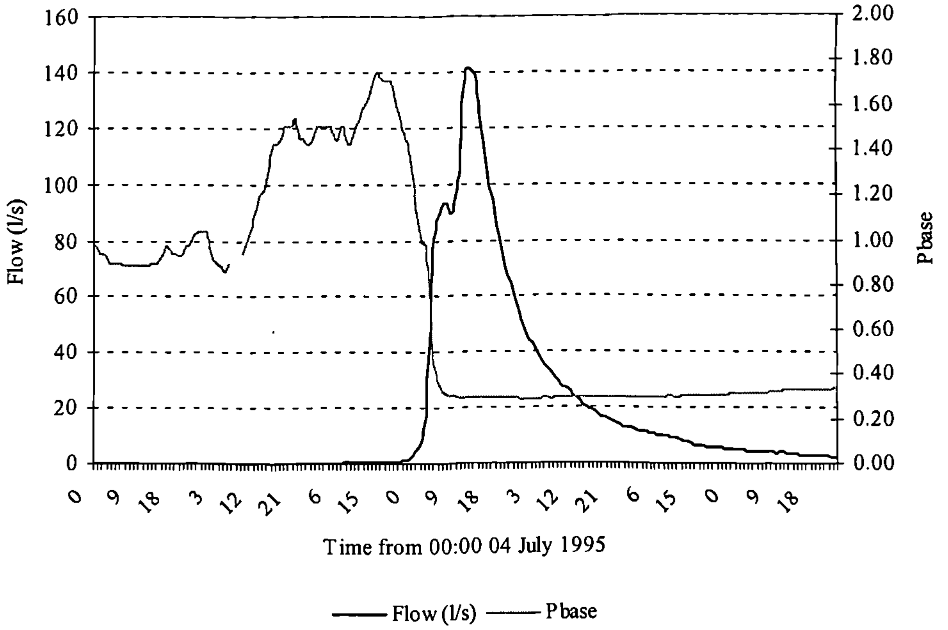
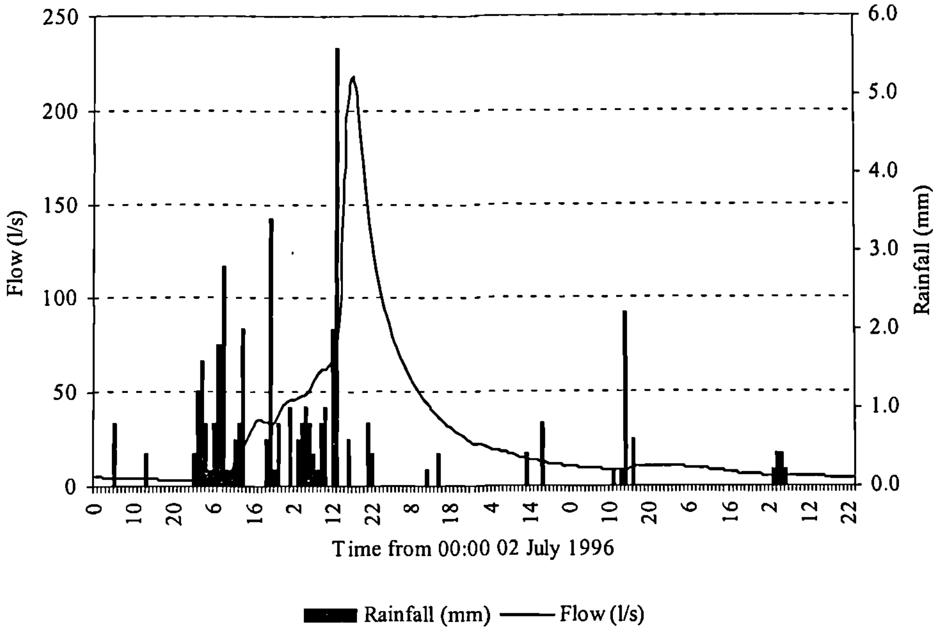


Appendix B7 Coalburn event 2 19 July 1995 flow and P_{base} time series



Appendix C Event 3 03 July 1996

Appendix C1 Coalburn Event 3 03 July 1996 flow and rain time series



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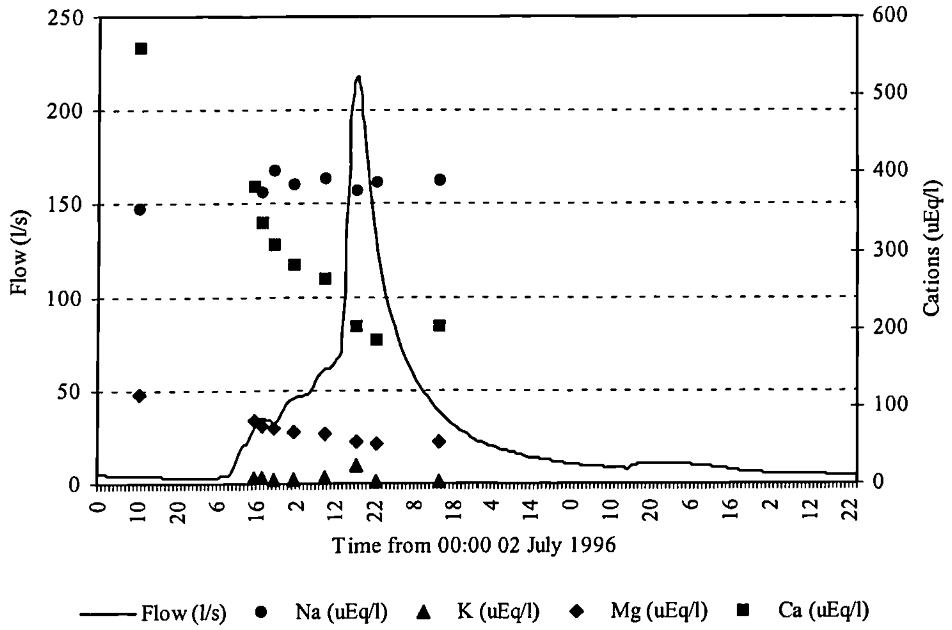

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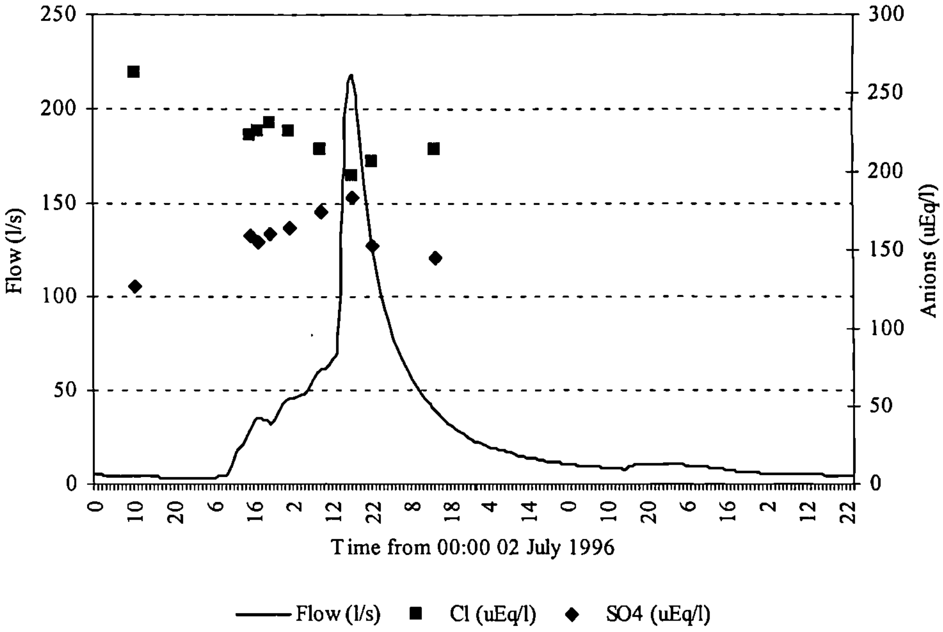

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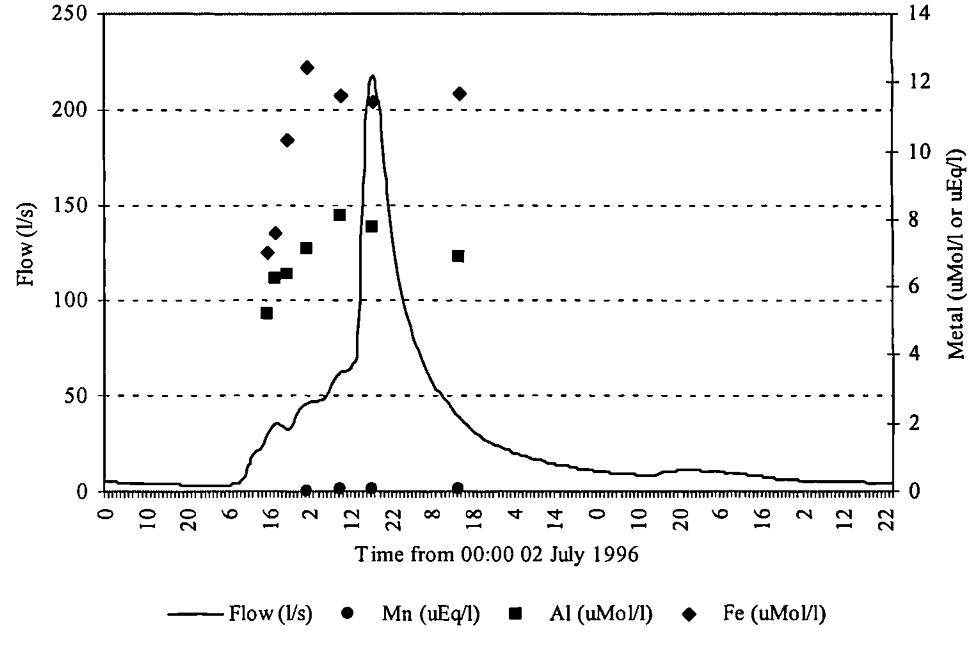
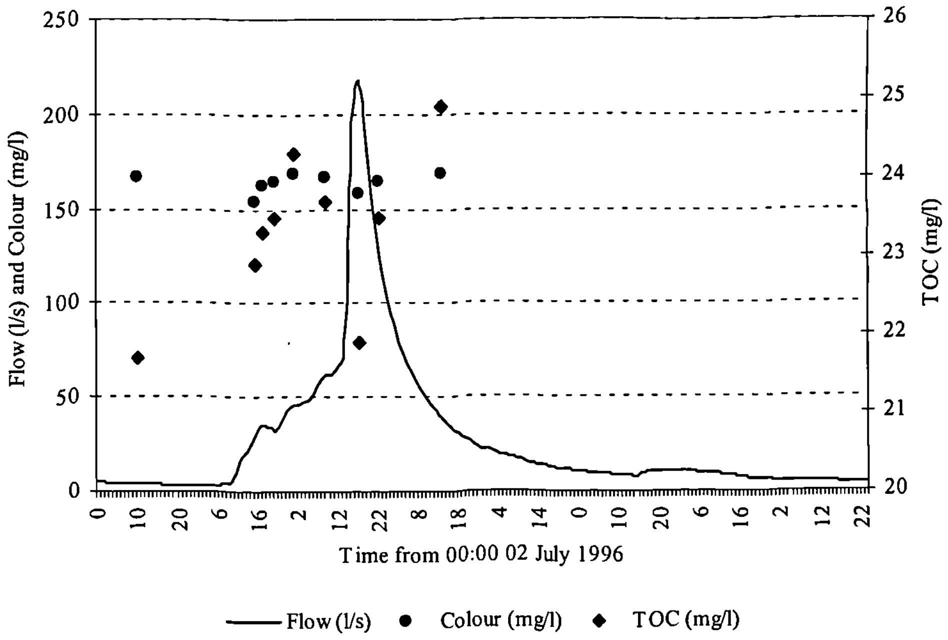


Appendix C5 Coalburn Event 3 03 July 1996 flow, colour and DOC time series



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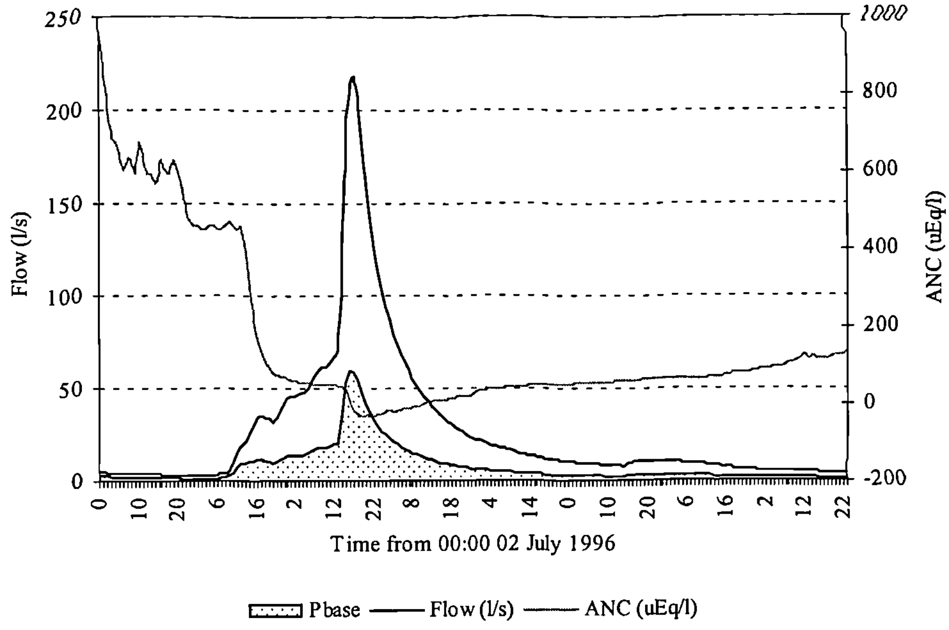

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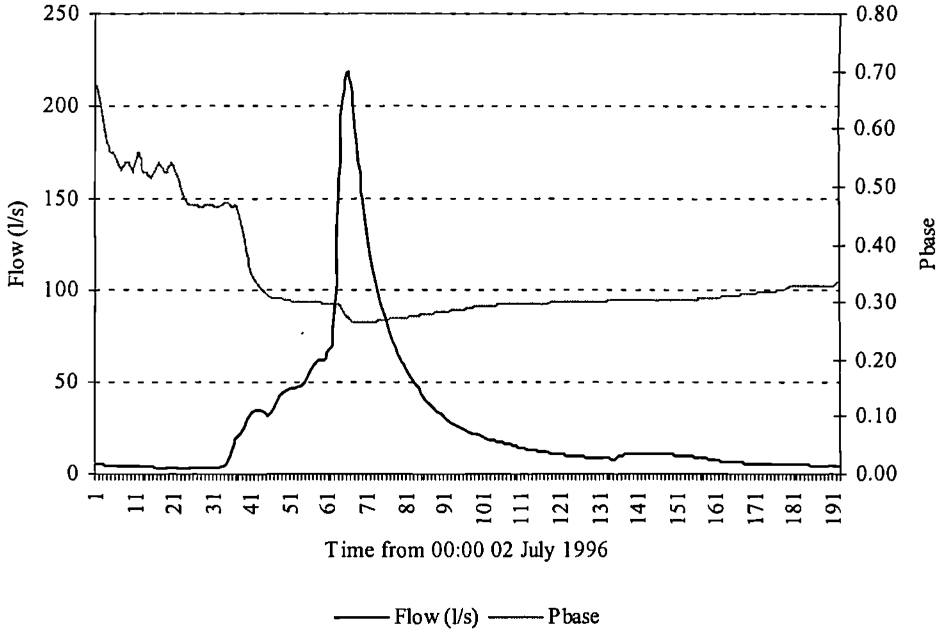
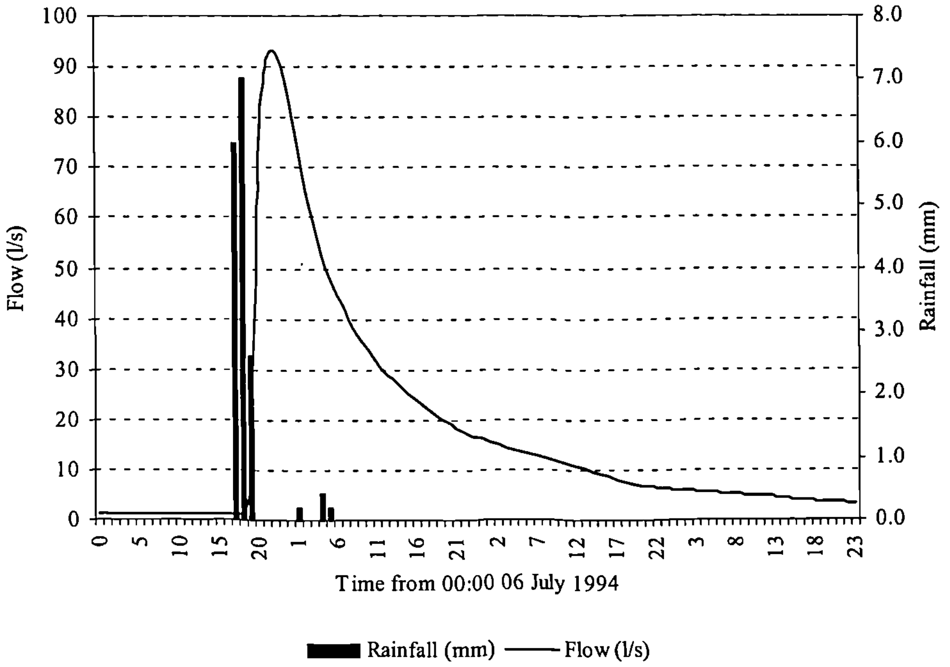


Appendix D Event 4 06 July 1994

Appendix D1 Coalburn Event 4 06 July 1994 flow and rain time series



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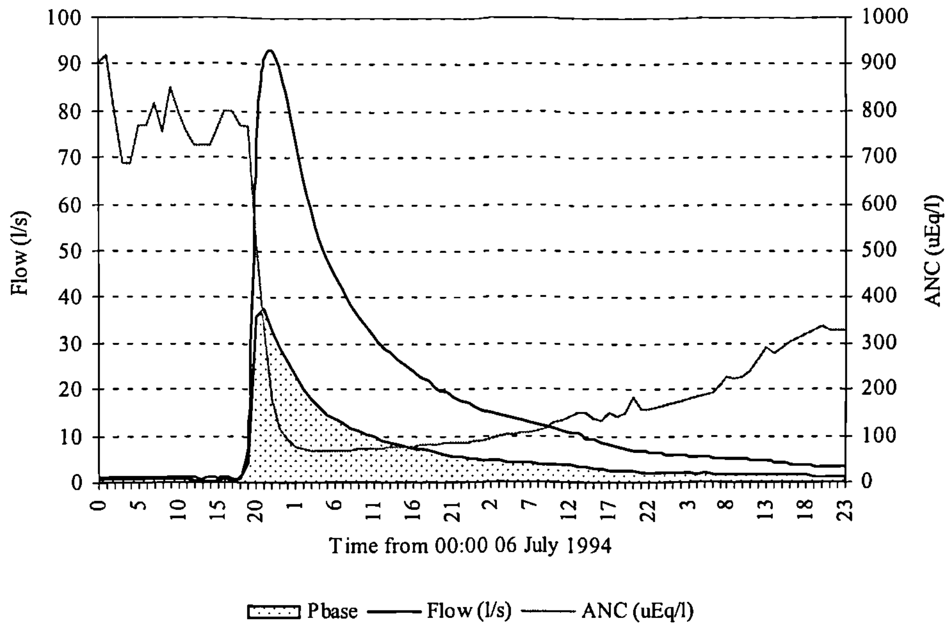

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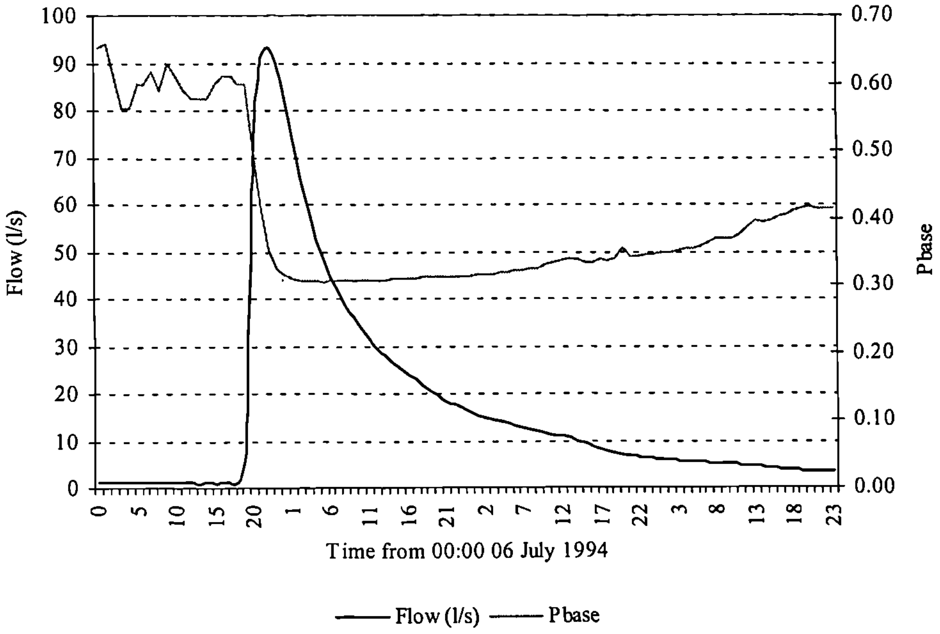
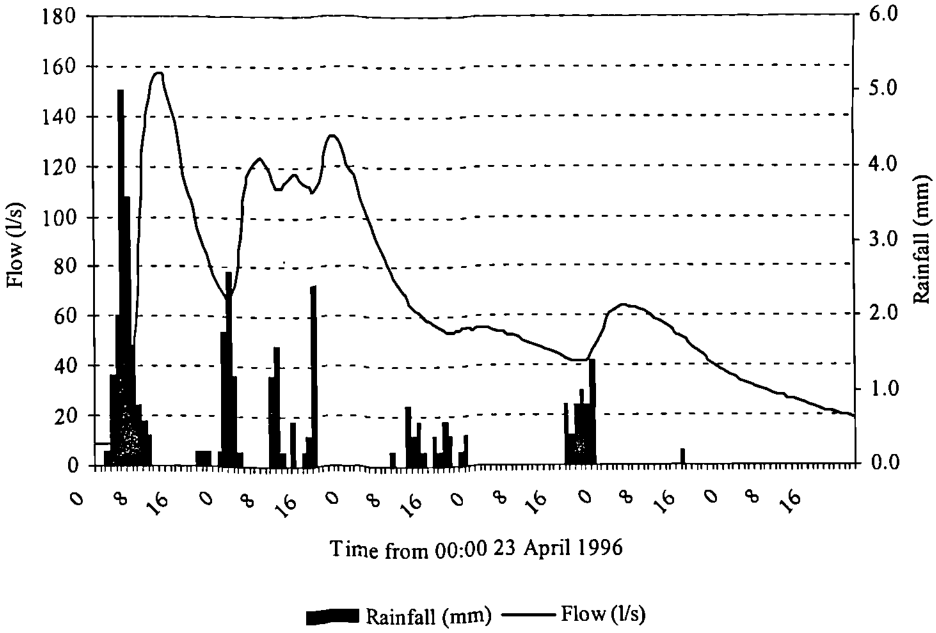


Appendix E Event 5 23 April 1996

Appendix E1 Coalburn Event 5 23 April 1996 flow and rain time series



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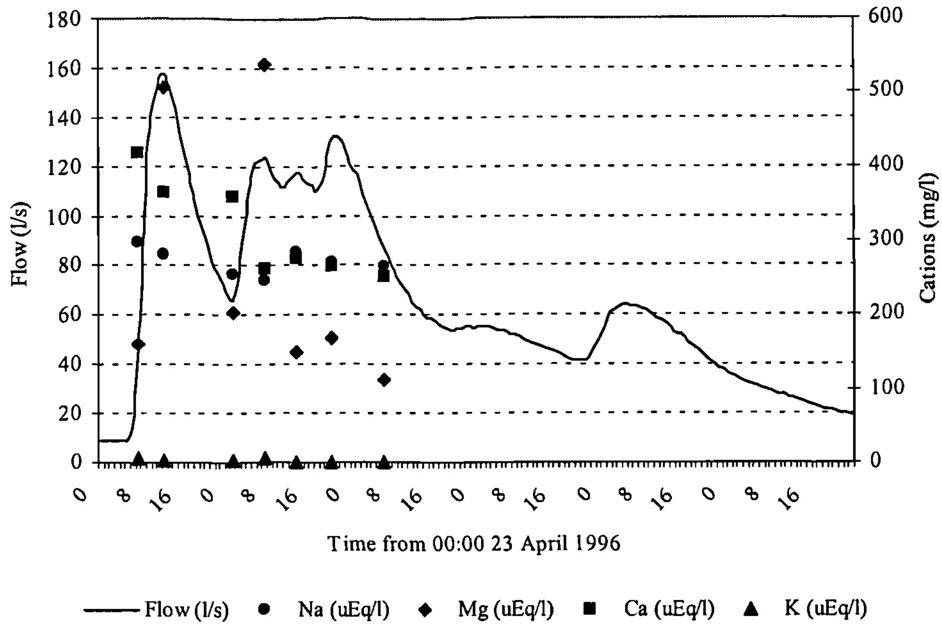

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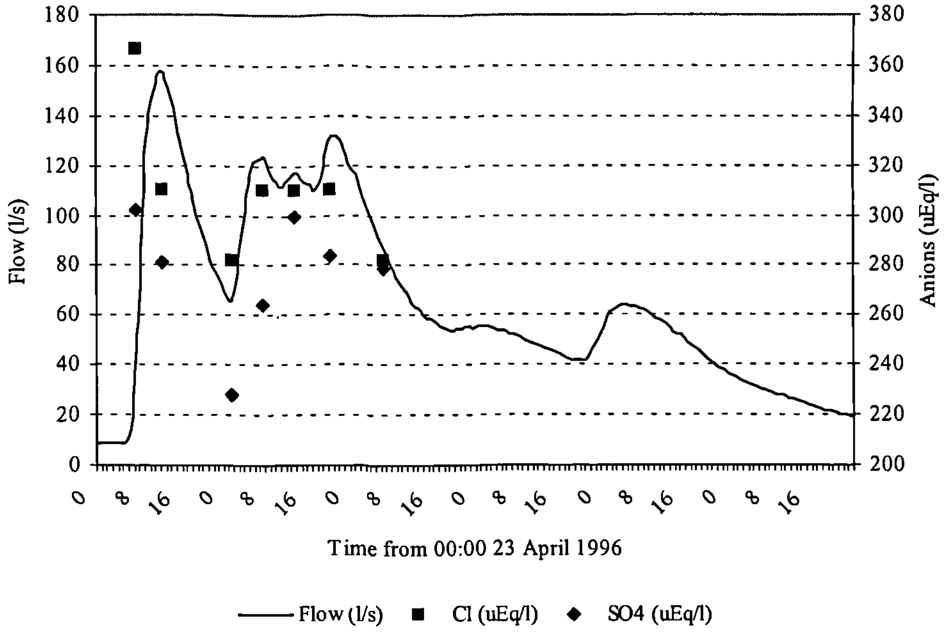

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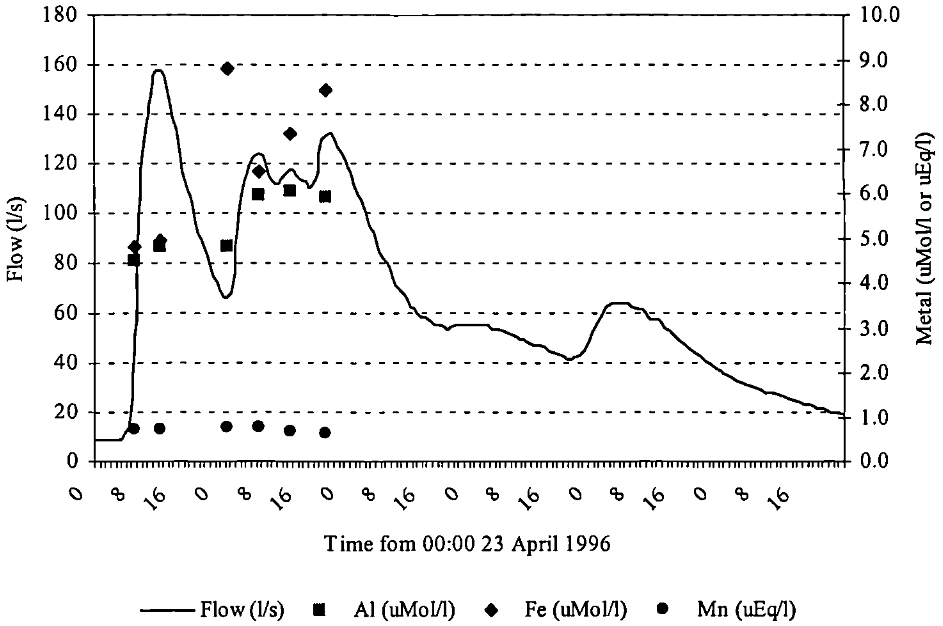

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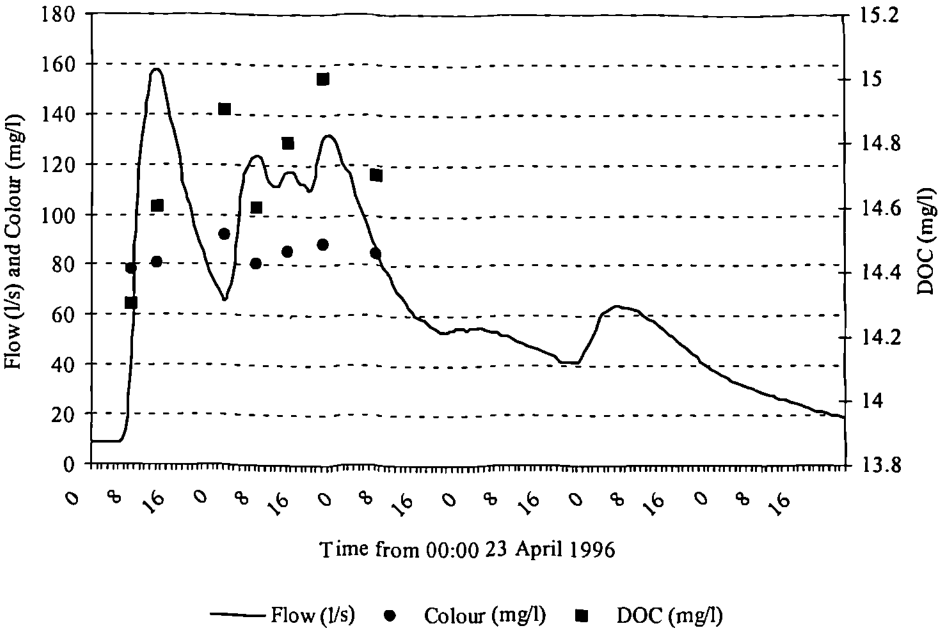

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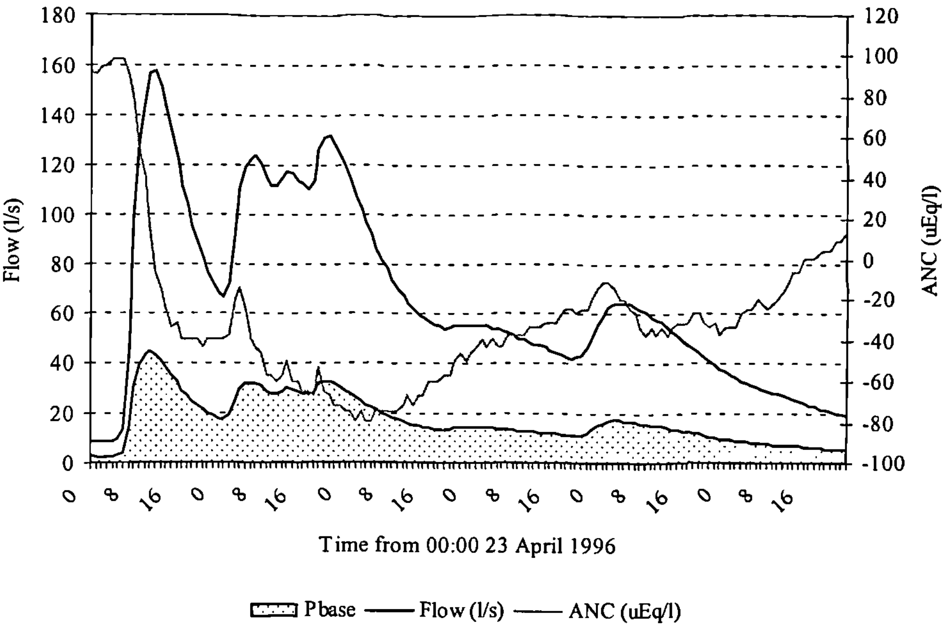

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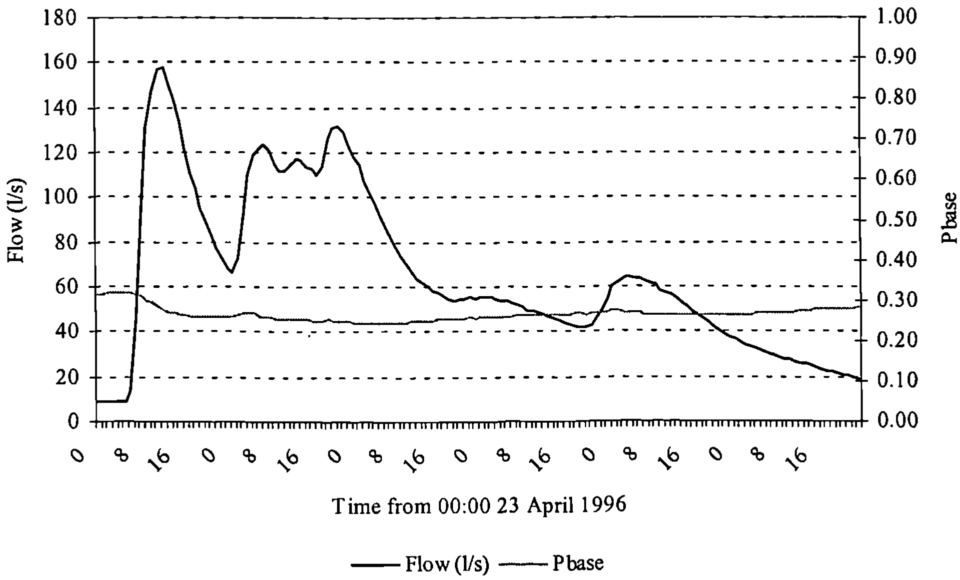
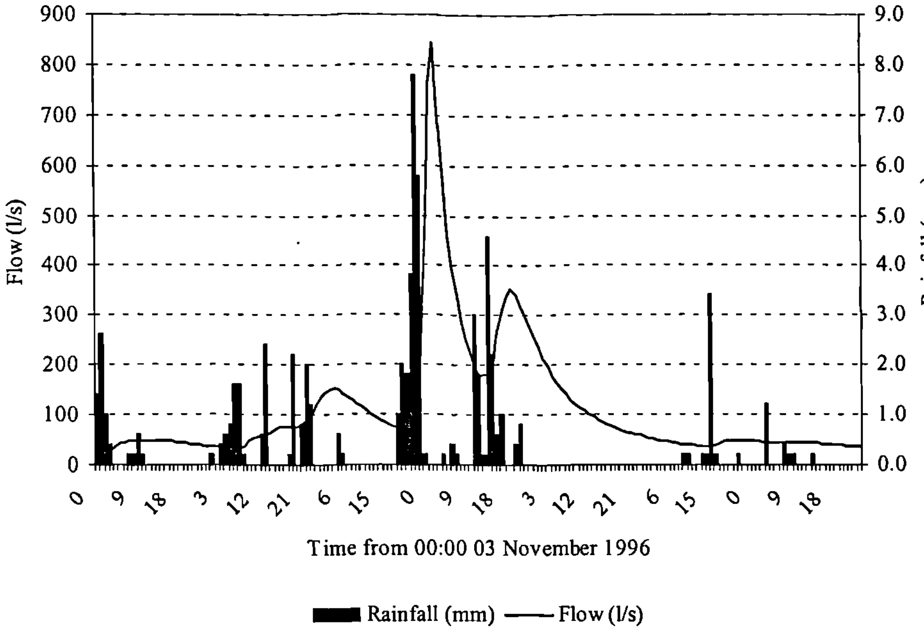


Appendix F Event 6 05 November 1996

Appendix F1 Coalburn Event 6 05 November 1996 flow and rain time series



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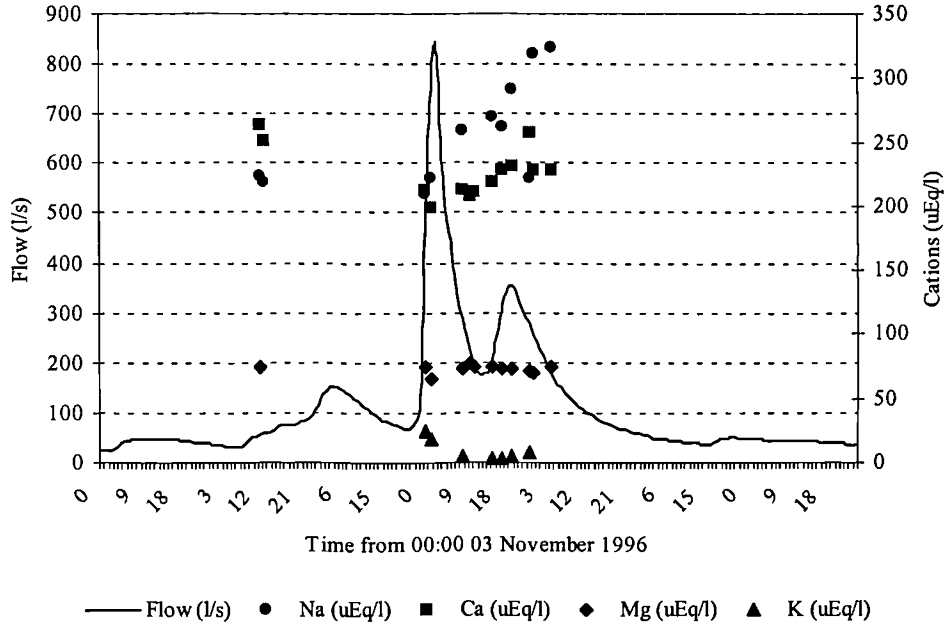

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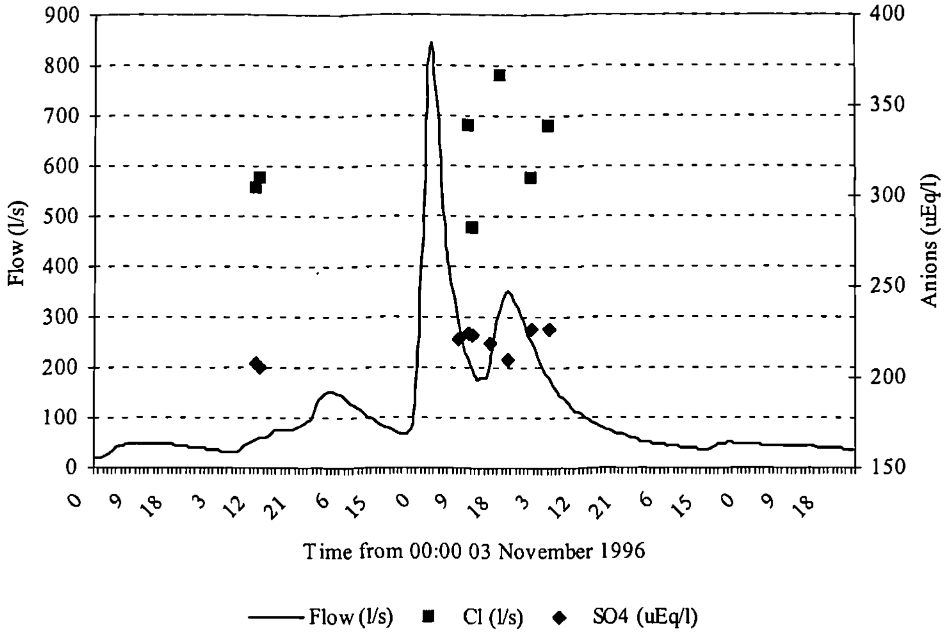

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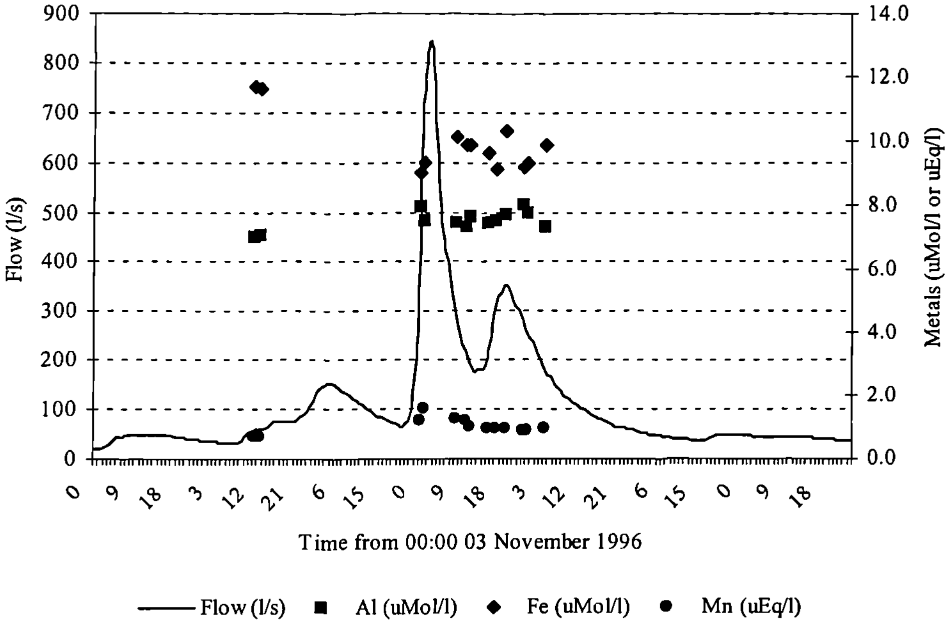
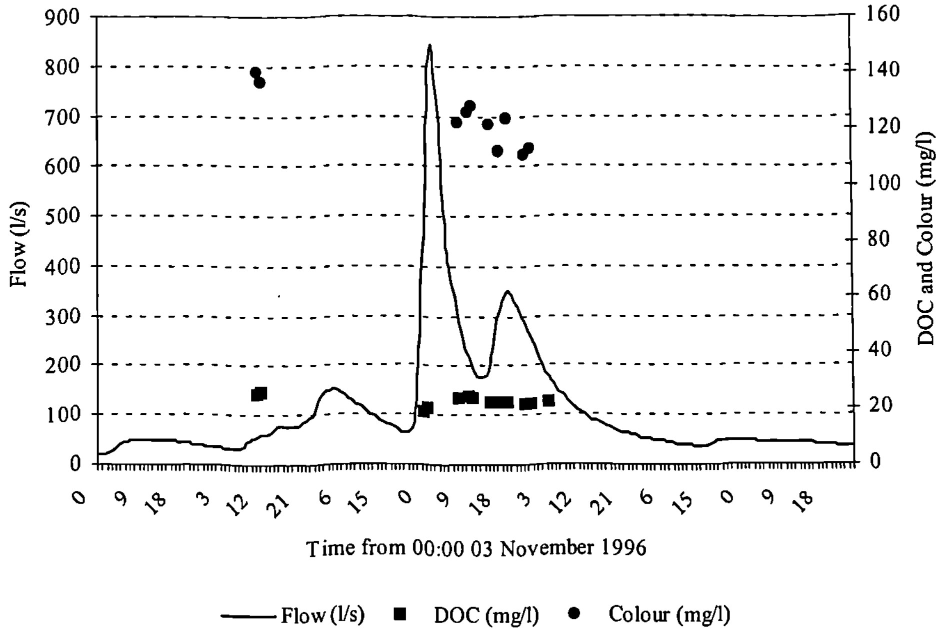


Appendix F5 Coalburn Event 6 05 November 1996 flow, colour and DOC time series



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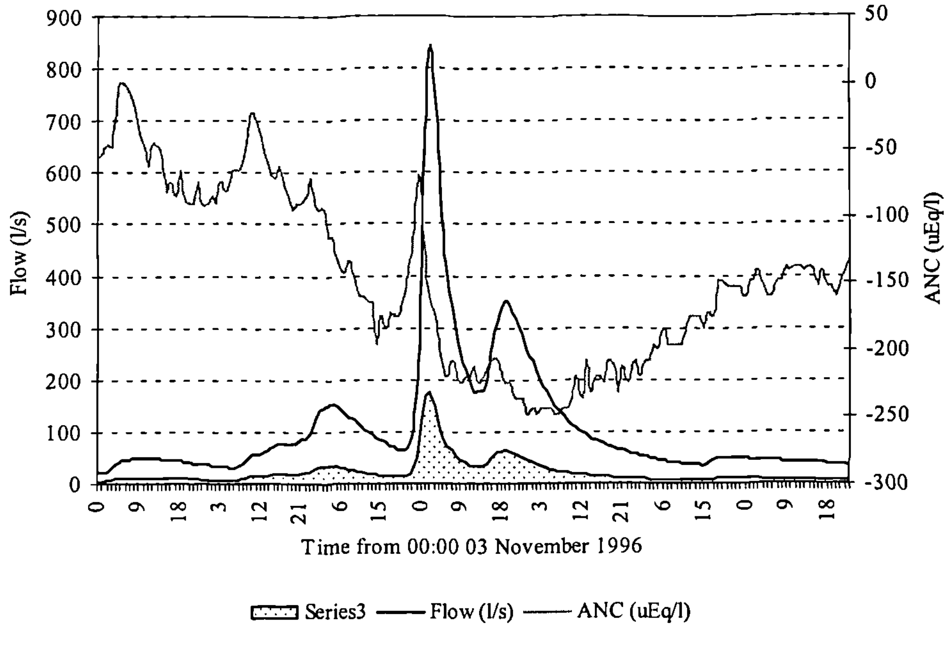
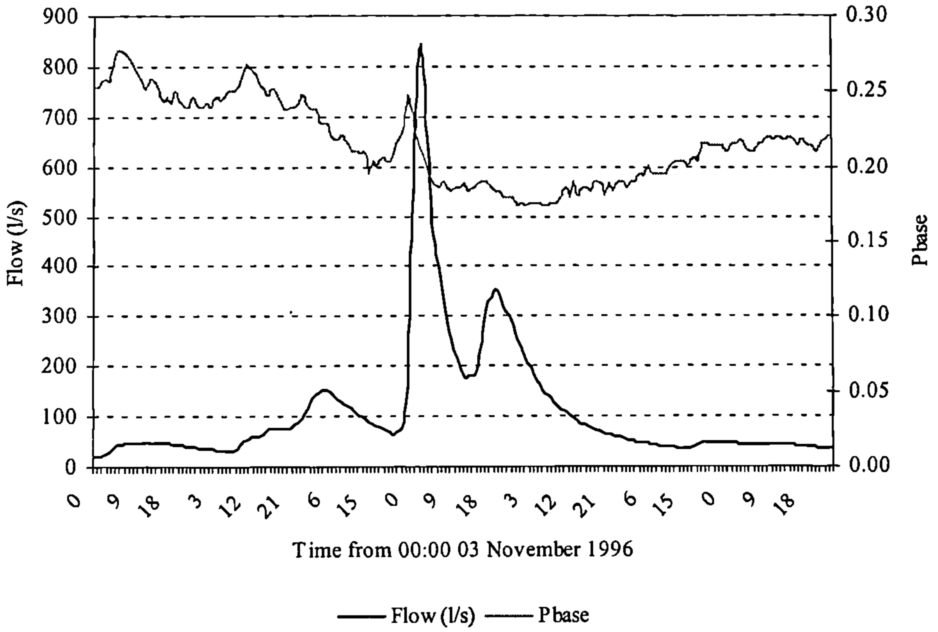
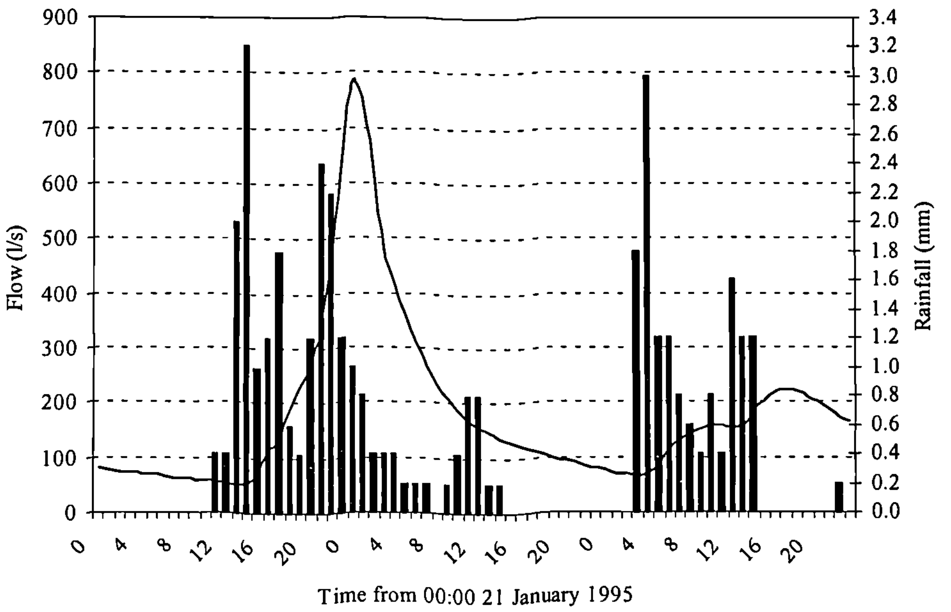


Appendix F7 Coalburn Event 6 05 November 1996 flow and P_{base} time series

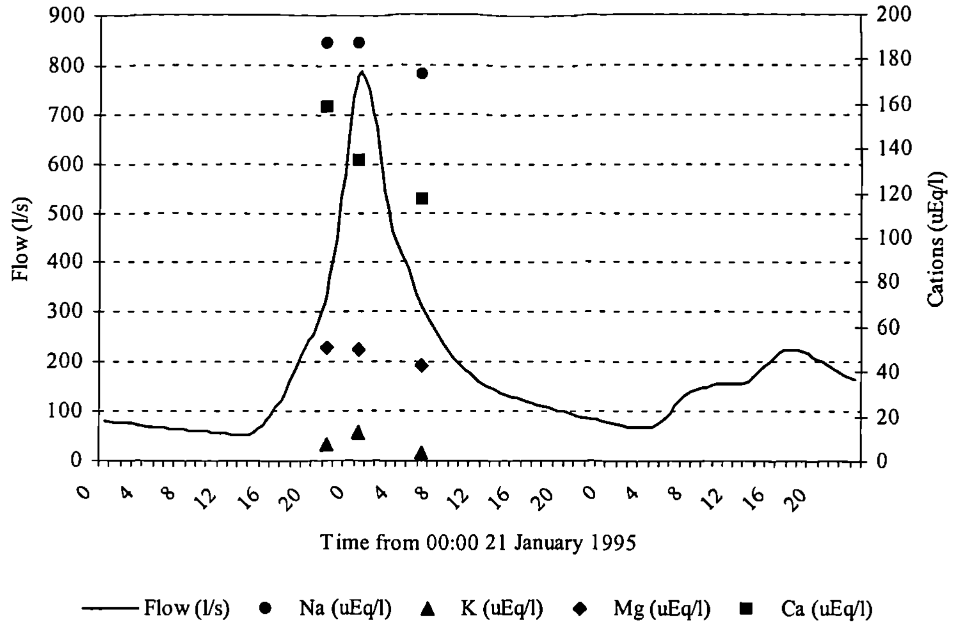


Appendix G Event 7 21 January 1995

Appendix G1 Coalburn Event 7 21 January 1995 flow and rain time series



Appendix G2 Coalburn Event 7 21 January 1995 flow and cation concentration time series



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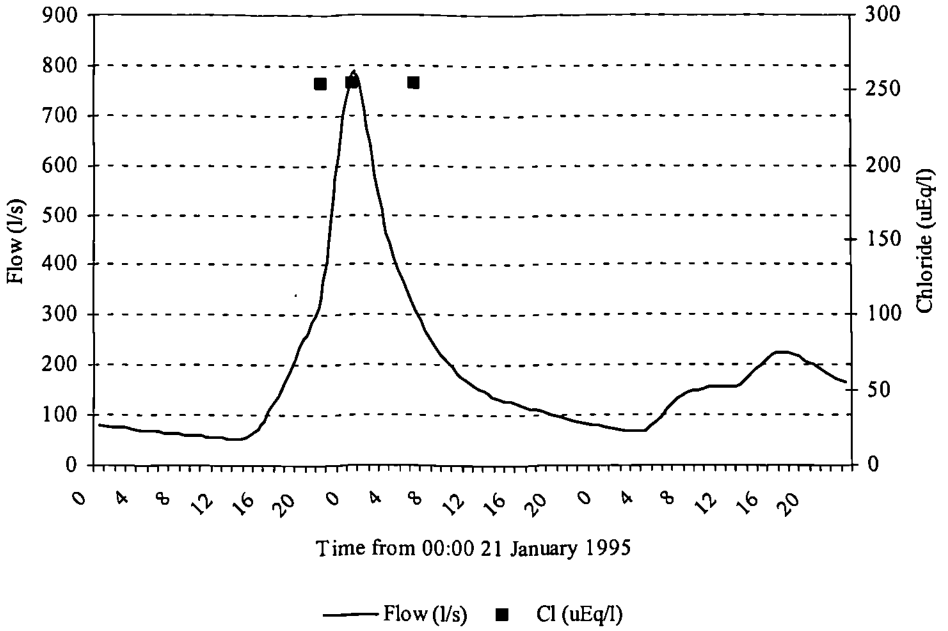
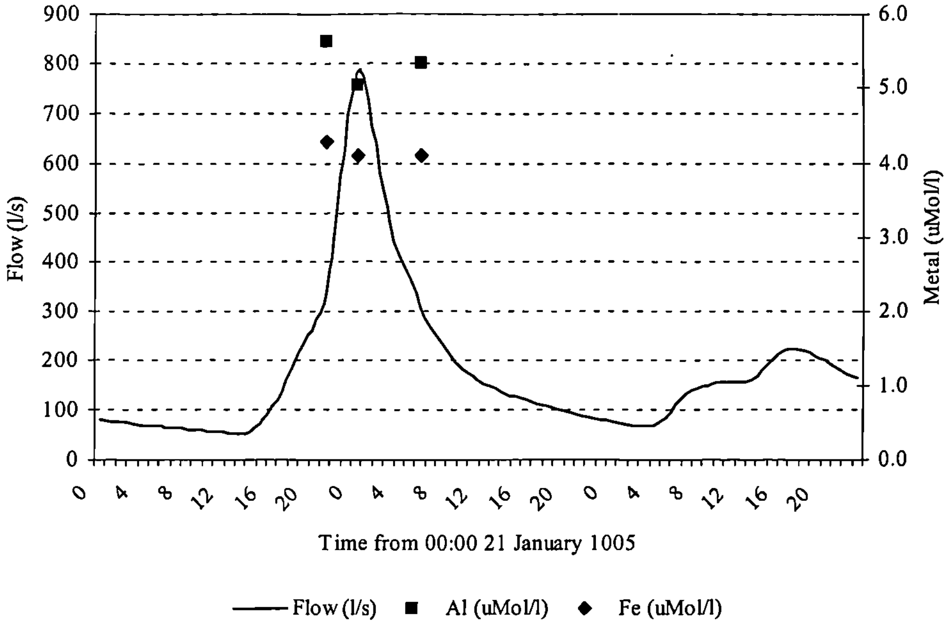
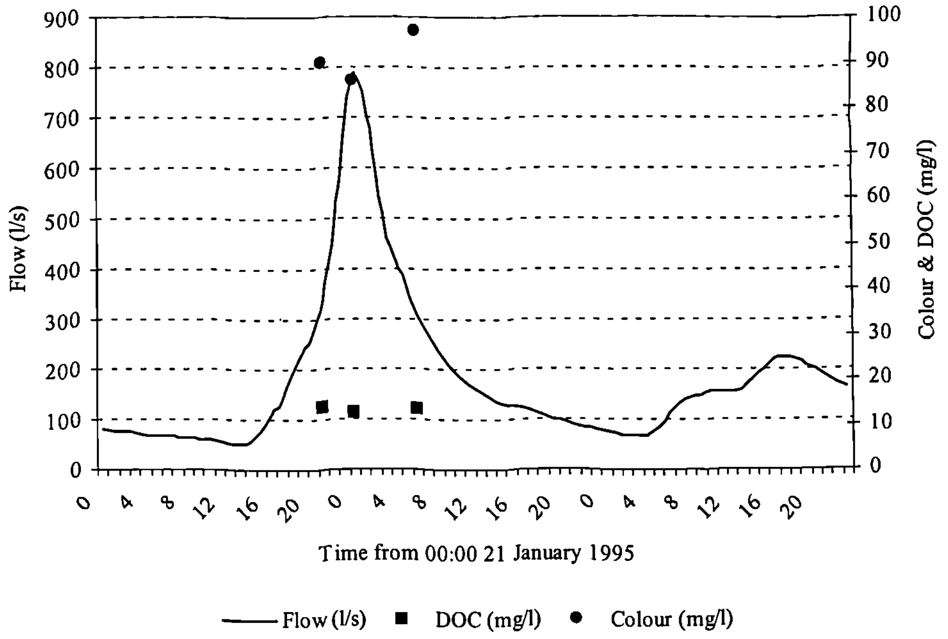


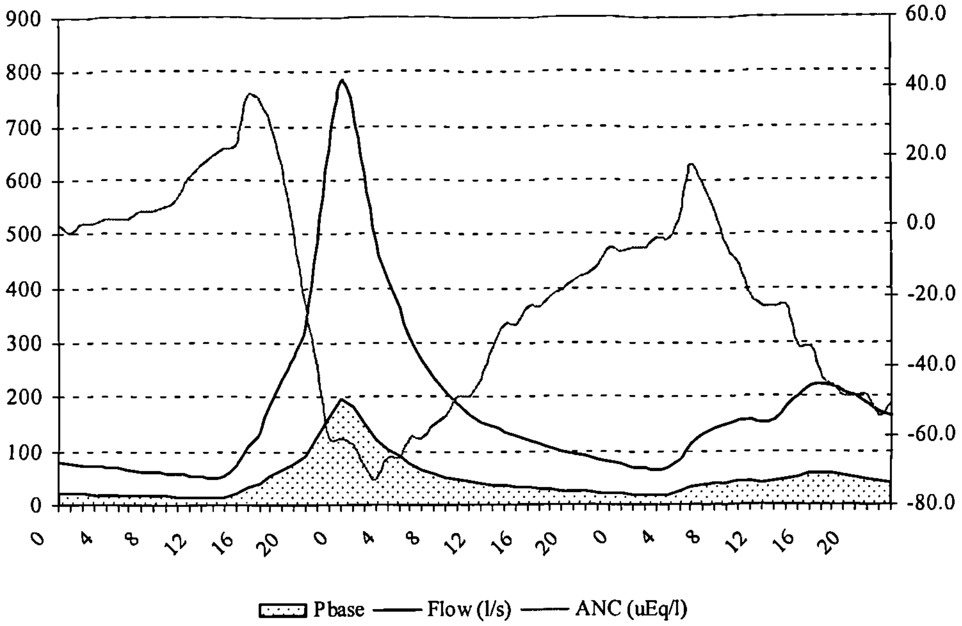
Appendix G4 Coalburn Event 7 21 January 1995 flow and metal concentration time series



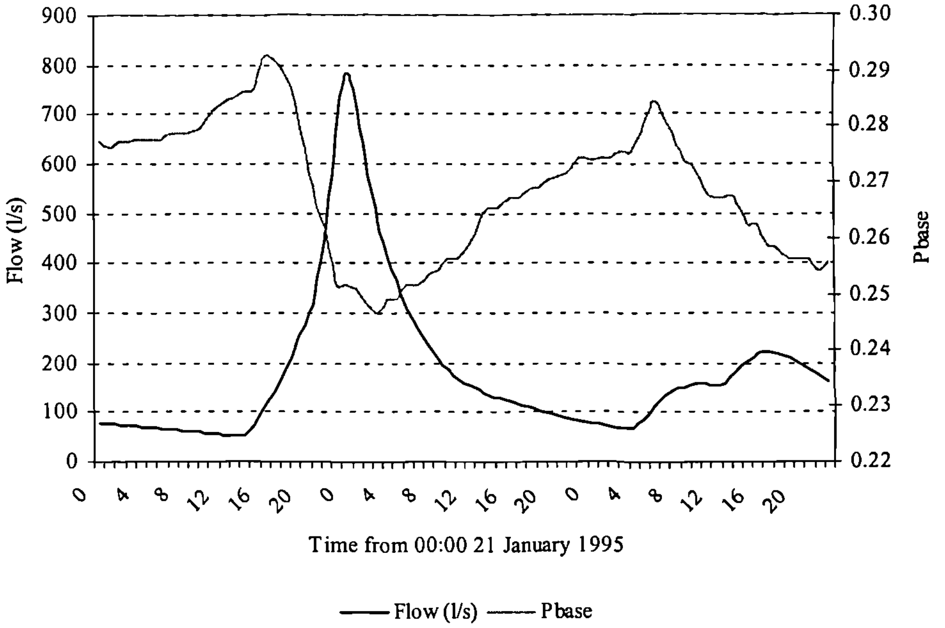
Appendix G5 Coalburn Event 7 21 January 1995 flow, colour and DOC time series



Appendix G6 Coalburn Event 7 21 January 1995 flow and ANC time series

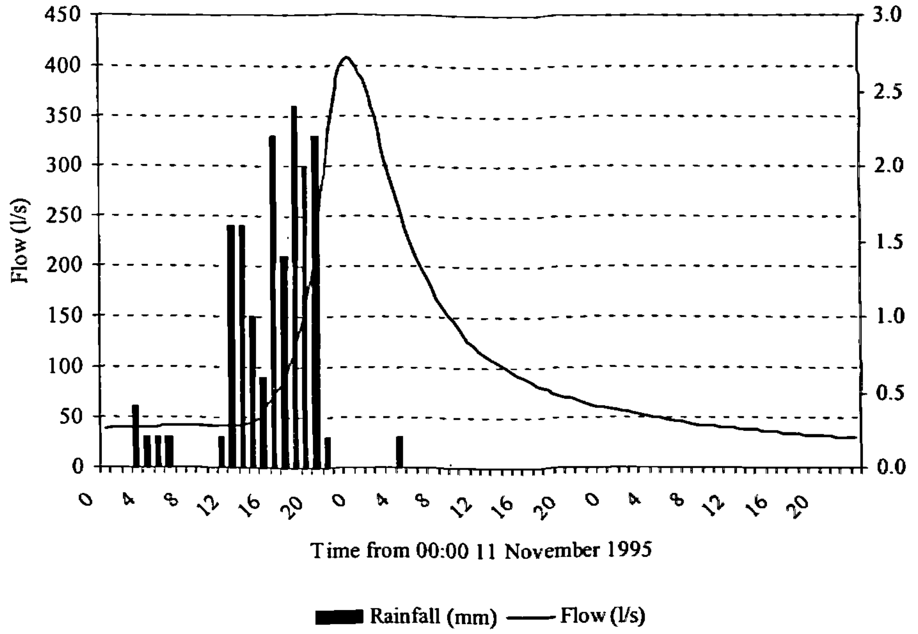


Appendix G7 Coalburn Event 7 21 January 1995 flow and P_{base} time series

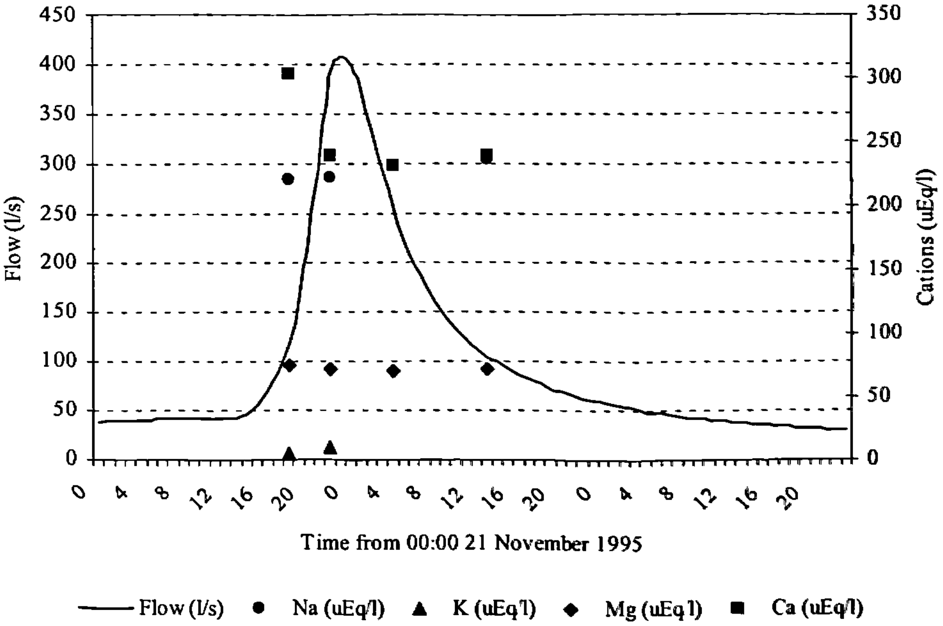


Appendix H Event 8 11 November 1995

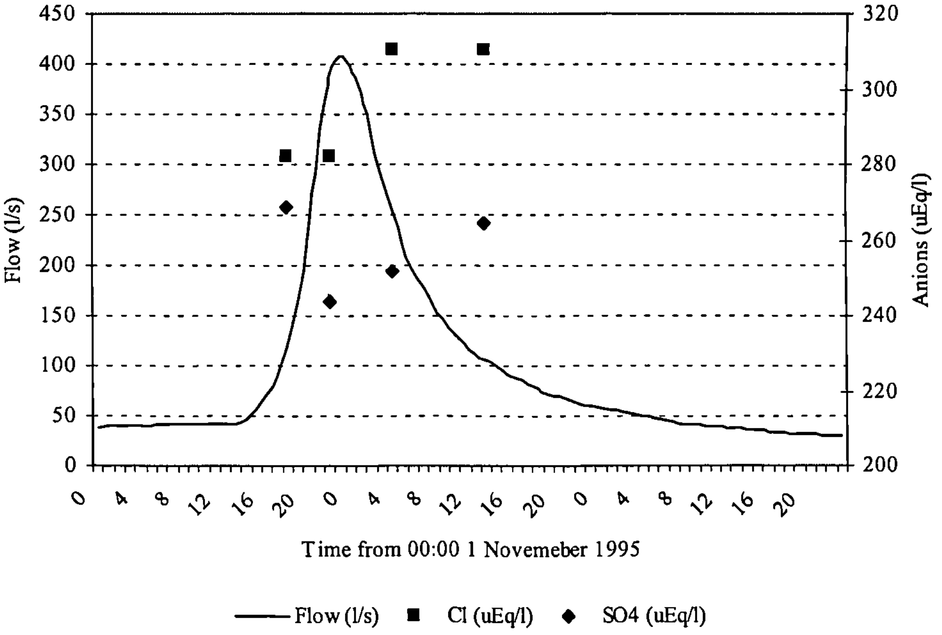
Appendix H1 Coalburn Event 8 11 November 1995 flow and rain time series



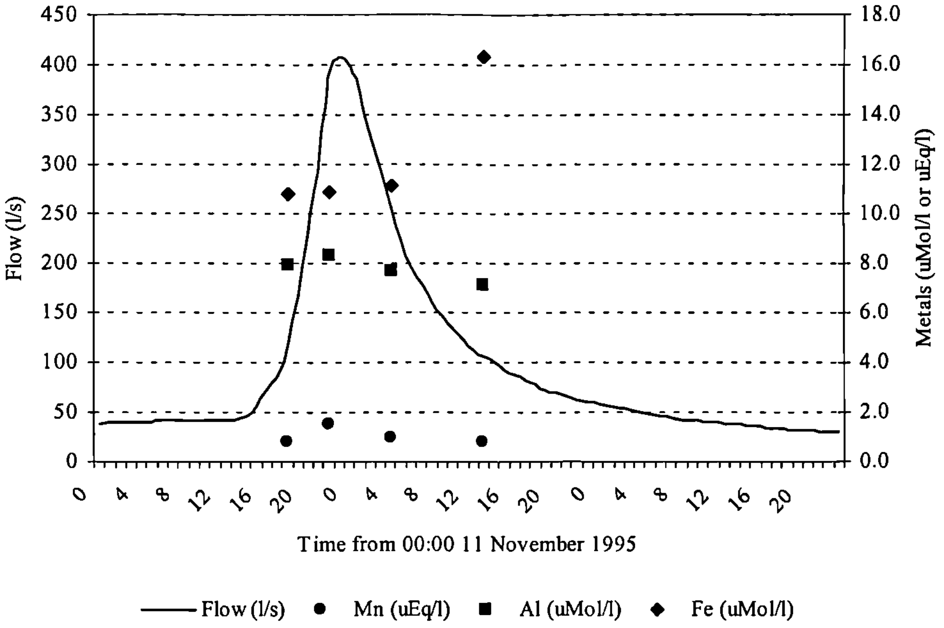
Appendix H2 Coalburn Event 8 11 November 1995 flow and cation concentration time series



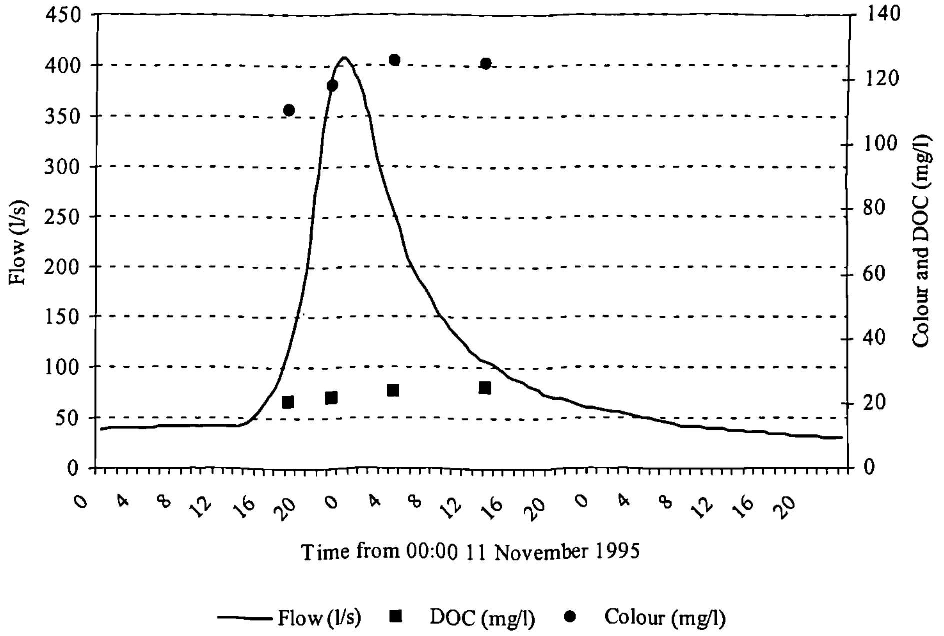
Appendix H3 Coalburn Event 8 11 November 1995 flow and anion concentration time series



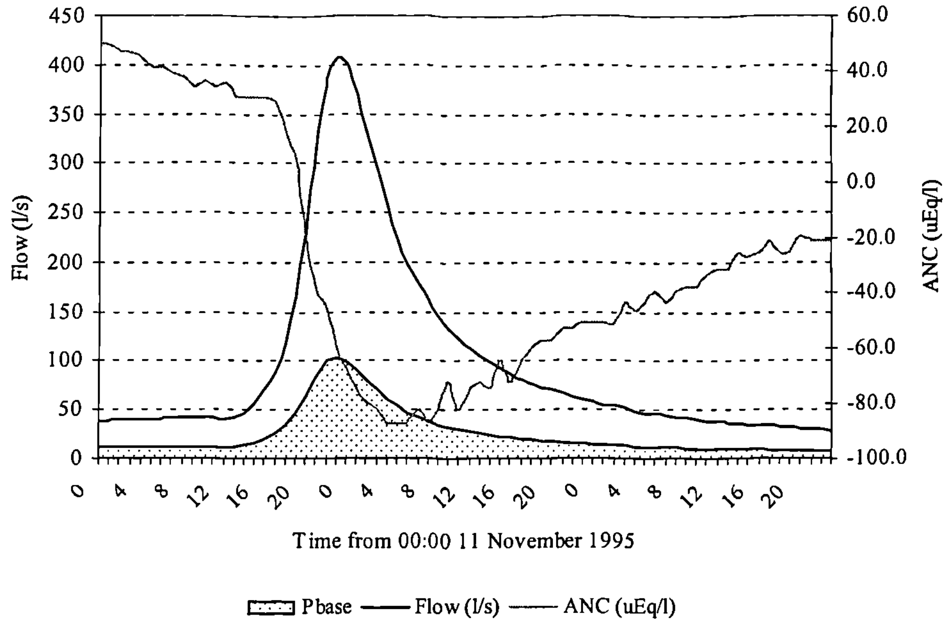
Appendix H4 Coalburn Event 8 11 November 1995 flow and metal concentration time series



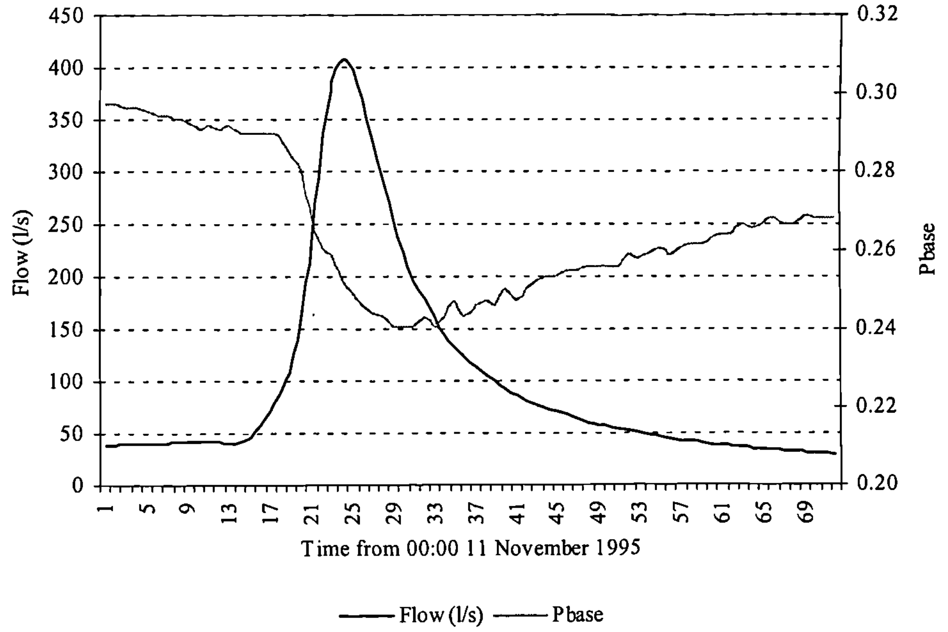
Appendix H5 Coalburn Event 8 11 November 1995 flow, colour and DOC time series



Appendix H6 Coalburn Event 8 11 November 1995 flow and ANC time series

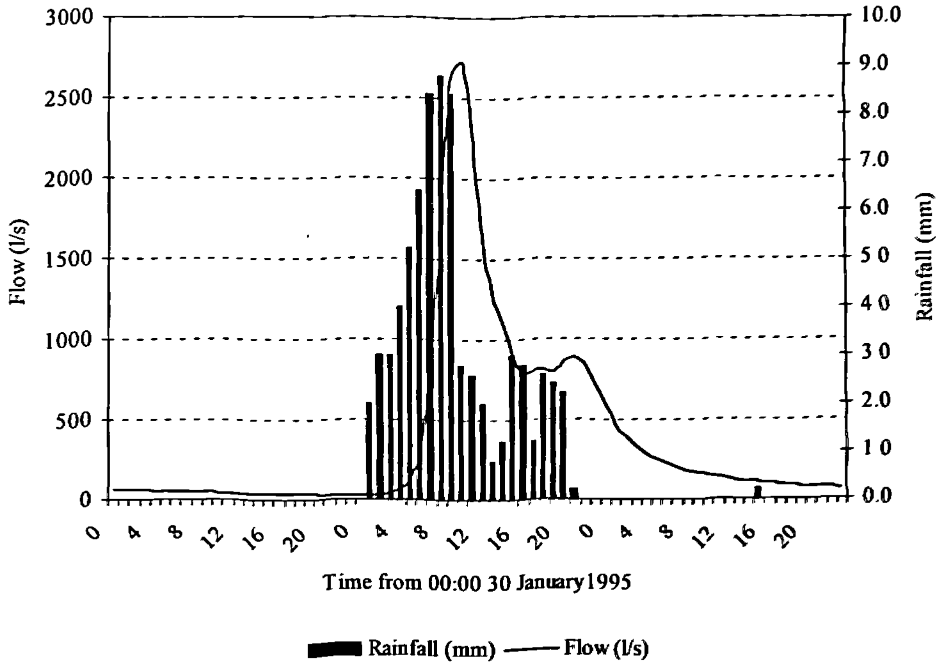


Appendix H7 Coalburn Event 8 11 November 1995 flow and P_{base} time series

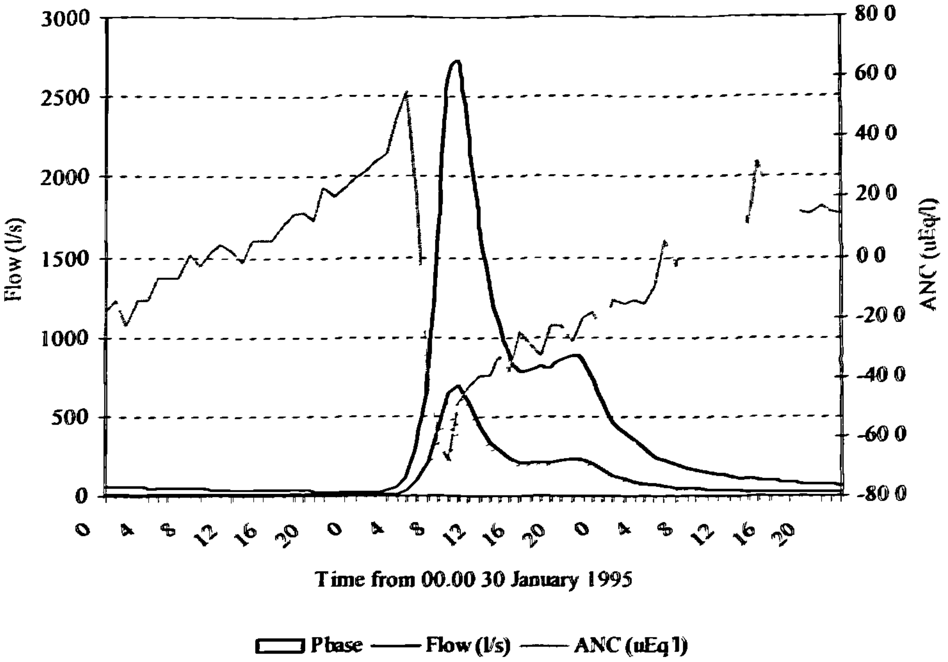


Appendix I Event 9 31 January 1995

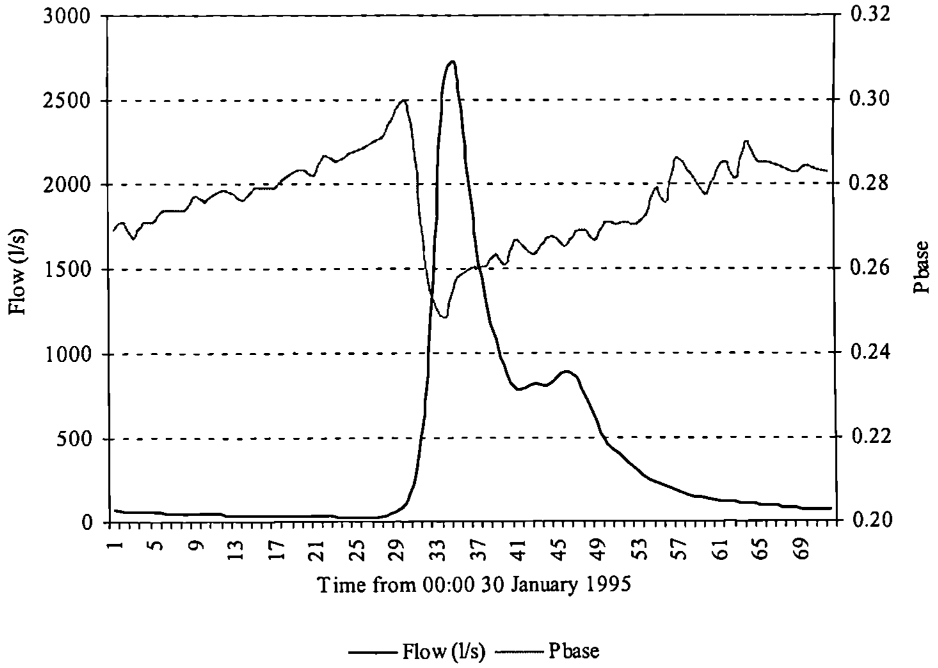
Appendix I1 Coalburn Event 9 31 January 1995 flow and rain time series



Appendix I2 Coalburn Event 9 31 January 1995 flow and ANC time series



Appendix I3 Coalburn Event 9 31 January 1995 flow and P_{base} time series



Appendix J Coalburn biological surveys

ENVIRONMENT AGENCY
NORTH WEST REGION
NORTH AREA
N. CUMBRIA ECOLOGY TEAM

TECHNICAL MEMORANDUM NB 583(1/99)

DATE 20 JANUARY 1999
AUTHOR R. R. PRIGG

NOTE ON FISH AND MACROINVERTABRATE SAMPLING COALBURN 5-11-98

BACKGROUND

The Agency has been contributing to a long term co-operative project to study the hydrological effects of upland afforestation in the Coalburn research catchment (Robinson et al., 1998). The recording of highly acidic episodes in the main stream during hydrological events lead to an investigation on impacts on stream biota (Prigg, 1994) and in 1998, Ray Moore requested further observations on the macroinvertabrate and fish populations of Coalburn. This report outline the findings of the survey done on 5-11-98, and refers to fish data generated by Fisheries department in 1994.

METHODS

The 5-11-98 fish survey was deliberately planned to be undertaken at the same season as the 4-11-93 survey, to attempt to minimise between survey differences due to movements within the catchment of spawning fish and other seasonal influences on in-situ stock. The survey was undertaken by electric fishing measured, stop netted sections of stream using a generator powered Electracatch pulsed DC electric fishing control box using a single anode. Population estimates were derived using a three catch removal methods and calculated using the Zippin method. All fish caught were measured, and subsequently returned unharmed to the survey reach.

Measurements of the wetted channel width in the survey length enabled the data to be expressed in terms of estimated fish numbers per unit area. Although no field weighing of fish was undertaken, a crude estimate of biomass density was derived by assuming a grossly oversimplified relationship between fish length and weight of the form: weight in gms = (length cms)^3 /100.

The macro invertebrate sampling was undertaken at two previously established sites just outwith the upstream and downstream limits of the fishing reach upstream of the gauging station, and at a new site below the gauging station. Sampling was by standard three minute kick sampling technique, catching invertebrates dislodged by kicking into the substratum in 1 mm mesh hand net. The kick sampling was supplemented by a 1 minute hand collection from stones, to more effectively sample those groups less vulnerable to capture by kick sampling. These samples were preserved and the organisms identified in the laboratory.

OBSERVATIONS AND DISCUSSIONS

Invertebrate species lists for the three sites sampled on he latest survey are attached, as are the 1993 finding for comparison. The fauna recorded at those sites sample din 1993 and 1998 is very similar, with a relatively diverse, Insect dominated fauna. There is a slight increase in the number of taxa recorded in the latest samples. Considered in terms of those taxa potentially sensitive to acidification stresses, all those initially recorded continue to be founds in the latest samples, and are now joined by the widespread but previously absent mayfly *Baetis rhodani*. Molluscs also now make an appearance on the species list.

Details of the results from the latest electric fishing survey are attached, and there is a separate table comparing results from all available fish survey data. The electric fishing results for the site sampled upstream of the gauging station in November 1993 and November 1998 show a clear decline in the trout population at the site, down now at what is a pathologically low density in the context of our Cumbrian hill stream data. It is tempting to point to the relative isolation of the small brown trout population in the limited catchment above the obstacle to upstream migration formed by the gauging structure, and their vulnerability to population decline from events like prolonged drought conditions, and possibly from impact on sensitive life stages of transient extreme acid events. In such an isolated population, any such losses could not be so well "buffered" by the subsequently better in-situ survival of offspring of upstream migrating spawning fish, which might otherwise be the case.

The availability of fish survey data from the Fisheries section for summer 1994, albeit surveyed by a method of single fishing without stopnets likely to lead to rather wider confidence limits in the estimate than from the multi-catch method used in 1993 and 1998, is interesting, and suggestive of the observed decline in the survey reach above the gauging station having occurred between 4-11-93 and 27-6-94.

There was no electric fishing below the gauging station in 1993, but both 1994 and 1998 data show a low density population, with evidence of successful recruitment, but with a biomass dominated by small numbers of old, mature fish.

CONCLUDING COMMENTS

The decline in the recorded trout density upstream of the gauging station between the 1993 and 1998 survey is interesting, but not in any sense reflected in the invertebrate findings, which show a slightly more diverse fauna with marginally increased representation of acid sensitive types. In trying to reconcile these observations, it is simplistic but possibly pertinent to draw attention to the relatively isolated status of the fish population in the upper catchment, with obstruction to aquatic upstream migrants, in contrast to the insect dominated invertebrate fauna, where e.g. the colonisation by aerial adults of *Baetis rhodani* could readily occur from downstream populations, or even outwith the catchment.

Although limiting flow impacts on the trout populations during the unprecedented prolonged drought situation of 95 and 96 would seem, on first principles consideration of the circumstances of the Coal Burn site, to be the most likely cause of any population decline, this view is difficult to sustain in light of 1994 Fisheries survey data. I understand that relevant pH, Al and Ca records would be available for 1993/4, and it would be worthwhile to examine these data for any evidence of potentially damaging acid events for trout, if only to rule out this limited possibility.

REFERENCES

Prigg R F (1994) Fish and macroinvertabrate population of Coalburn, and their interpretations in an acidification context. NRA NW Region North Area Technical Memorandum NB 276(2/94).

Robinson M, Moore R E, Nisbet T R and Blackie J R (1998) From moorland to forest: the Coalburn catchment experiment. Institute of Hydrology Report No. 133.

SPECIES LISTING FOR SELECTED INVERTEBRATE SAMPLES 1998

Site No	290	290	290
Decimal	51	52	53
Method	1	1	1
Year	98	98	98
Month	11	11	11
Day	05	05	05
Taenopteryx nebulosa	A	A	
Protonemura sp	B	C	B
Amphinemura sp	B	A	B
Nemoura sp	B	B	B
Leuctra sp	B	C	B
Perlodidae	A	A	A
Chloroperlidae	A	A	A
Baetis rhodani	A	A	A
Leptophlebiidae	B	B	B
Rhyacophila sp	A	A	A
Polycentropidae	B	B	B
Limnephiledae	B	B	B
Goeridae	A	A	A
Hytiscidae		A	
Hydraenidae	B	A	A
Helodidae	B	A	
Elmis aenae	B	B	B
Esolus sp		B	
Limnius volckmari	B	B	B
Oulimnius sp	B	B	B
Sialis sp	A	A	A
Tipulidae	A	A	
Dicranota sp	B	A	A
Ceratopogonidae		A	
Chironomidae	B	A	B
Empididae	A	A	A
Hydracarina	A		A
Planobidae		A	
Sphaeridae	A	A	
Tubificidae	A	A	A
Lumbricidae	A	A	
Total Taxa	27	30	22
Trent biotic index	11	12	11
CDC index			
BMWP score	122	130	104
ASPT value	6.42	6.19	6.5
Inferred NWC class			

Key to site numbers listed above

290.51 NY695779 Coal Burn 170m US gauging station.
290.52 NY694778 Coal Burn 100m US gauging station.
290.53 NY693777 Coal Burn 80m DS gauging station.

Key: Relative abundance figures in the body of table

A=1-9 specimens, B=10-99 specimens, C=100-999 specimens, D=1000-9999 specimens, E =>9999 specimens

SPECIES LISTING FOR SELECTED INVERTEBRATE SAMPLES 1993

Site No	290	290
Decimal	51	52
Method	1	1
Year	93	93
Month	11	11
Day	04	04
Taenopteryx nebulosa	2	2
Protonemura sp		1
Protonemura meyeri	2	3
Amphinemura sulcicollis	2	2
Nemoura avicularis		2
Leuctra hippopus	2	4
Leuctra nigra	1	
Perlodes microcephala	1	1
Isoperla grammatica	3	3
Chloroperla torrentium	1	
Paraleptophlebia submarginata	2	2
Rhyacophila dorsalis	2	1
Plectrocnemia conspersa	2	2
Polycentropus flavomaculatus	2	
Limnephiledae	2	2
Silo pallipes		1
Hydraena sp	2	2
Helodidae	1	2
Elmis aenae	3	4
Limnius volckmari	2	2
Oulimnius sp	4	3
Tipulidae	1	
Pedicia rivosa		2
Dicranota sp	2	2
Chironomidae	2	2
Simuliidae	2	2
Empididae	1	1
Collembola	2	2
Tubificidae	1	
Erpobdella octoculata		1
Total Taxa	25	25
Trent biotic index	11	11
CDC index		
BMWP score	106	108
ASPT value	6.63	6.75
Inferred NWC class		

Key to site numbers listed above

290.51	NY695779 Coal Burn 170m US gauging station.
290.52	NY694778 Coal Burn 100m US gauging station.

Key: Relative abundance figures in the body of table

1=1-9 specimens, 2=10-99 specimens, 3=100-999 specimens, 4=1000-9999 specimens, 5 =>9999 specimens

ELECTRIC FISHING SURVEY RESULTS

Site Coal Burn 100m US gauging station
Date 05-11-98
Length fished 70m
Mean width 1.16m
Area fished 81.2 square m.

Fish	Catch 1	Catch2	Catch 3	Total	Estimate	Efficiency	Confidence Limits
Trout 0+	0	1	0	0	>1		
Trout 1++	2	1	0	3	3	71%	3+/-1

Comments: Re. trout0+ - minimum estimate – no Zippin estimate possible.

Density (area)

	Numerical density fish/sq. m.	Crude biomass density gms/sq.m.
trout0+	>0.016	>0.03
trout 1++	0.047	5.51
salmonid (total)	>0.063	>5.54

Density (linear)

	Numerical density fish/sq. m.	Crude biomass density gms/sq.m.
trout0+	>0.018	>0.03
trout1++	0.054	6.23
salmonid (total)	>0.072	>6.26

Summary fish length data

	Range	Mean	Standard Deviation	n
trout 1++	211-238	226.0	11.2	3

ELECTRIC FISHING SURVEY RESULTS

Site Coal Burn 20m DS gauging station
Date 05-11-98
Length fished 56m
Mean width 1.13m
Area fished 63.3 square m.

Fish	Catch 1	Catch 2	Catch 3	Total	Est efficiency
trout0+	0	1	0	1	>1

Comments: Re. trout0+ - minimum estimate – no Zippin estimate possible.

Density (area)

	Numerical density fish/sq. m.	Crude biomass density gms/sq.m.
trout0+	>0.012	>0.04
salmonid (total)	>0.012	>0.04

Density (linear)

	Numerical density fish/sq. m.	Crude biomass density gms/sq.m.
trout0+	>0.014	>0.04
salmonid (total)	>0.014	>0.04

SUMMARY OF COAL BURN ELECTRIC FISHING SURVEY DATA

SITE	DATE	LENGTH SAMPLED	MEAN WIDTH	0+ TROUT DENSITY	1++ TROUT DENSITY	METHOD
US GAUGING STATION	4-11-93	67m	1.02m	0.015	0.249	III
	27-6-94	45m	1.07m	-	0.039	I
	5-11-98	70m	1.16m	>0.012	-	III
DS GAUGING STATION	27-6-94	45m	1.36m	0.064	0.03	I
	5-11-98	56m	1.13	>0.016	0.047	III

Notes

i) fish density figures are expressed as estimates of fish per square metre.
ii) method indicates sampling as follows:
  I single fishing, no stopnets, standard calibration figure used for estimate.
  III three fishing, stopnets used, estimate based on Zippin method.

NRA

NORTHERN AREA BIOLOGY LABORATORY
CARLISLE

TECHNICAL MEMORANDUM

Copies to:

R E Moore
N C Durie
L B Hughes
S Douglas
M Diamond, RFH

Subject Fish and macroinvertebrate populations of Coalburn, and their interpretation in an acidification context

Date 21/2/94 Author R F Prigg Biol file: NB276(2/94)

BACKGROUND

The Coalburn catchment on the Upper Irthing has been the subject of a long term study, commenced in 1966 by the Institute of Hydrology, the Forestry Commission and the Cumberland River Authority, to examine the hydrological effects of upland afforestation and drainage.

The work is on-going as an N.R.A. R and D project terminating April, 1994.

Recent work by University of Newcastle has examined aspects of surface water acidification in the catchment, and shown up acid events in the main stream during hydrological events.

This preliminary biological investigation was requested by project leader Ray Moore to investigate the possible impact on the stream biota of the acidic water chemistry regime that had been demonstrated.

METHODS

Fish and invertebrate sampling was undertaken on 4th November, 1993.

Fish sampling was by electric fishing, using an Electracatch WFC911 portable battery operated electric fishing unit, set for smooth DC, high volts. The 70m reach electric fished was stopnetted at upstream and downstream limits, and sampled by a three catch removal method. Fish caught were measured, and ultimately returned unharmed to the survey reach at the completion of the sampling.

The fish catch data was used to provide an estimate of population in the stopnetted reach by the Zippin method. Field measurements of the wetted channel width of the stream in the sample area enabled the data to be expressed as fish density in terms of number per unit area. By assuming a grossly oversimplified relationship between fish length and weight of the form $\text{Wt gms} = (\text{length cms})^3/100$, crude estimates of biomass density could also be expressed. Note that these biomass density estimates, in our experience of juvenile salmonid population in hill streams are likely to underestimate actual values, but represent a reasonable way of 'boiling down' length data to give some indication of biomass for comparative purposes, in the absence of field weighings.

The results of the fish sampling are presented as Appendix 1, in the form of a print out from our computerised fish survey archive.

The macro-invertebrate sampling was undertaken at two locations just outwith the upstream and downstream limits of the electric fished reach. The two sites were each sampled using a 3 minute kick sample, catching invertebrates dislodged by kicking into the substratum in a 1mm mesh hand net. The kick sampling was supplemented by a 1 minute hand collection from stones, to more effectively sample those groups less vulnerable to capture by kick sampling. The samples were preserved, and the organisms identified in the laboratory. The species lists of invertebrates found are presented in Appendix 2.

In addition to the fish and invertebrate sampling, general field notes on the physical habitat characteristics of the sites, and on the aquatic flora were made, and retained on file.

OBSERVATIONS AND DISCUSSION

The only fish species present in the sample reach was brown trout (<u>Salmo trutta</u>). We have considerable data on salmonid populations of hill streams, including acidified sites in Cumbria, and the density recorded in this instance is an unexceptional moderate value in terms of 1+ and older salmonid density (see, for example comparative data in Appendix 3), certainly in no way pathologically low, such as we found (Prigg R.F. 1983) in many acidified hill streams in the very poorly buffered Upper Esk and Duddon catchments and some nearby catchments (see Appendix 4).

Scales for age determination were not taken from the trout captured, but from our knowledge of growth rates of trout in local hill streams, and inspection of the trout length-frequency distribution, it was apparent that only one 0+ fish was captured, a specimen of 57mm length. Visual observations during the electric fishing sampling indicated that one similar sized trout escaped capture.

The presence of at least one fish from the current years hatching of ova at least signifies some successful recruitment in the current year. The fact that the population in the sampled reach was dominated by 1+ and older fish, with a low contribution from 0+ fish, is not necessarily a reflection of poor recruitment. The stream is small and narrow, and although offering considerable cover by virtue of undercut banks etc., it is likely that under low flow conditions the fish distribution would be restricted largely to residual pools etc., and in such restricted habitat the fry of the year would be likely to suffer high predation by older trout.

Although not systematically sampled as part of our survey reach, a large natural deep pool upstream of the survey reach, with a maximum depth in excess of one metre, was informally electric fished from its margins to see if any older, larger trout were present. Only fish of comparable size to those taken in our survey reach were noted, though it is likely that with the equipment we were using sampling in this deep awkward situation was not very effective.

The gauging weir downstream of our sample reach would act as a barrier to upstream migrants, and on the day of our survey several medium sized adult trout, c. 200mm length were seen immediately below the structure.

Turning to the invertebrate sampling results, an immediately striking observation is the relative lack of Ephemeroptera in the sample, particularly the common and widely distributed Baetidae and Heptageniidae. The only mayfly species present was Paraleptophebia submarginata; in our experience the Leptophlebidae are relatively acid tolerant. Molluscs and crustaceans are also lacking. It is instructive to apply an indicator system developed by members if the Catchment Research Group at Cardiff in 1989 (Rutt G.P. et al 1990) that was designed to detect acidic stress in upland streams throughout Britain, from a knowledge of the macroinvertebrate fauna (see Appendix 5). Strictly this method is recommended for application for sampling carried out between January and mid May, as the system was based on kick samples taken in Winter and Spring when the faunal relationship with acidity is most pronounced. Our samples were taken in November, but would be expected to be reasonably approximate to a faunal list for the recommended seasonal period.

The acid sensitive families Baetidae, Heptageniidae and Hydropsychidae were absent, so the samples both fall into groups 3 or 4. Both include Taeniopterygidae, Elminthidae and Perlodidae, so the final diagnosis is group 3. As can be seen from Appendix 5 this group 3 was characterised in the national data set (derived from Welsh, Scottish and N.W. Region data) as acidic stream; 71% with pH <6.0, 87% with filterable aluminium $>50ugl^{-1}$, 53% with Al $>100ugl^{-1}$. They were poorly buffered; 76% with total hardness $<10mgl^{-1}$, 95% with hardness $<15mgl^{-1}$. The faunas were described as impoverished, and the streams thought to be vulnerable to enhanced acidification by conifer forestry.

In considering these generalisations against the chemical regime in Coalburn, reference was made to a review of the Coalburn catchment experiment (Robinson M. and Hind P. D. 1990) and to data sheets on monthly snap chemical samples (samples examined were taken between 2.3.92 and 4.10.93). Robinson and Hind reported mean pH at the main weir as 5.9. Arithmetic means pH in the monthly snap samples examined was 5.82, from 20 observations with a range 4.2 - 7.2 (geometric mean pH was 5.04).

Clearly Coalburn conforms to the typical mean pH grouping of Group 3 sites. Data on Ca, Mg, total Aluminium, and unacidified filtered aluminium were also examined in the monthly snap samples. It was immediately and not unexpectedly clear that there was a close relationship between pH, and calcium and magnesium levels, low pH's being associated with high discharge conditions in which the calcium and magnesium levels were diluted, the catchment rather than rainfall being the prime source of these ions. The calcium and magnesium levels covered a wide range; mean calcium level was 7.93ml/l, with a range of 2.9 to 28.3 in 18 monthly observations. The mean magnesium level was 1.14mg/l, with a range of 0.49 to 3.5mg/l, again from 18 records.

Converting these calcium and magnesium means to total hardness, we get a mean total hardness for the period of 24.6mg/l as $CaCO_3$. This value is significantly in excess of the typical hardness of group 3 streams which have 95% with a hardness $<15mg/l^{-1}$ as $CaCO_3$.

Moving to aluminium records, there was less data, but for total aluminium eleven records ranged from 90 to 275ug/l with a mean of 139ug/l. Unacidified, filterable aluminium had even fewer records in the period with just 3 examined, ranging from 96 to 159 ug/l with a mean 115ug/l. However, it is apparent that Coalburn appears to fall within the aluminium concentration range criteria of group 3 sites.

One saving grace of the Coalburn water chemistry in the acidification context in terms of the impact on fish, is the moderate as opposed to extremely low calcium level. In fact the Upper Irthing catchment generally, in an area of underlying Carboniferous rocks, with boulder clay deposits, is not one we would think of in terms of particular geological sensitivity. In those central Lake District streams where we have witnessed significant restriction of salmonid populations, the streams have very low calcium levels and the impact on the fish is reasonably attributable to the toxicity of elevated levels of soluble monomeric aluminium at pH's around 5 in the presence of very low calcium concentrations. The fundamental difference in the chemical regime between the Coalburn site and our comparably acidic but low calcium central Lake District sites is highlighted in Appendix 6. Note also that the fishless sites in the Upper Esk and Duddon catchment and adjacent systems were also in areas of very high rainfall (mostly well in excess of 2200mm/year), greater than the annual mean of 1200mm for Coalburn area. The other significant factor likely to be ameliorating any aluminium based toxic impacts on fish in Coalburn is the presence of peat staining; the presence of humic materials gives the potential for organic complexing of aluminium, with resulting toxicity reduction.

Our routine biological quality monitoring of the Upper Irthing catchment, which for obvious strategic reasons concentrates on main river and major tributary sites, rather than smaller headwater streams (which would be expected to be more vulnerable to precipitation - induced water chemistry fluctuations), gives no general cause for concern in these larger watercourses. Invertebrate data from the two nearest routine sites on the Irthing upstream and downstream of the Coalburn confluence are presented in Appendix 7. The greater diversity at the upstream, Churnsike site, is very likely a reflection of physical differences between the two sites, with clay exposures at Churnsike encouraging a diverse and abundant macroflora; in terms of presence of potentially acidication sensitive taxa however, note, eg. the abundance of Gammarus and sensitive Ephemeroptera at both sites.

Moving to smaller tributary sites, Appendix 8 includes data gathered between 1987 and 1990 from four Upper Irthing tributaries, which are no longer included as routine monitoring sites. Inspection of the species lists shows expected seasonal fluctuation but the lack of Baetidae in Spring 1990 other than at Foulbog Sike is striking. Foulbog Sike also is the only one of the four with Gammarus present. The Padda Burn site appears, on the strength of presence/absence of acid sensitive taxa, to be the most acidified of the four, with Winter/Spring samples more often than not assigning it to group 3 of the classification of Rutt et al, the group to which Coalburn was assigned by our sampling.

SUGGESTIONS FOR FURTHER WORK

We plan to undertake some further invertebrate sampling of Coalburn to look at the fauna in other seasons, and to ensure a sample is taken within the January to mid May sampling period recommended by Rutt et al for applying their indicator key.

Although the fish stock is currently not showing any gross indications of acidification impact, the existence of significant rapid low pH excursions, albeit in a water not dramatically low in calcium, would be of interest to investigate further. This is particularly relevant in the context of work on the survival of freshly fertilised eggs of brown trout by Brown D.J.A. and Lynam S. 1982 which showed some mortality occurring during 8 day exposure at some combinations of calcium and pH levels which have been (instantaneously) recorded in the Coalburn monthly snap sampling programme. For example, snap sampling on 3.11.92 gave pH 4.2 and Ca 3.5mg/litre. Such extremes are probably of relatively short duration, and unlikely to equate to the eight days exposure results quoted, which at this pH and calcium level would result in under 60% survival after 8 days by interpolation in Brown and Lynams results. Nevertheless, the rapid onset of conditions in potentially lethal ranges is clearly worthy of further consideration, and suggestions to undertake egg box experiments on trout ova in the catchment seem most appropriate.

R F PRIGG

REFERENCES

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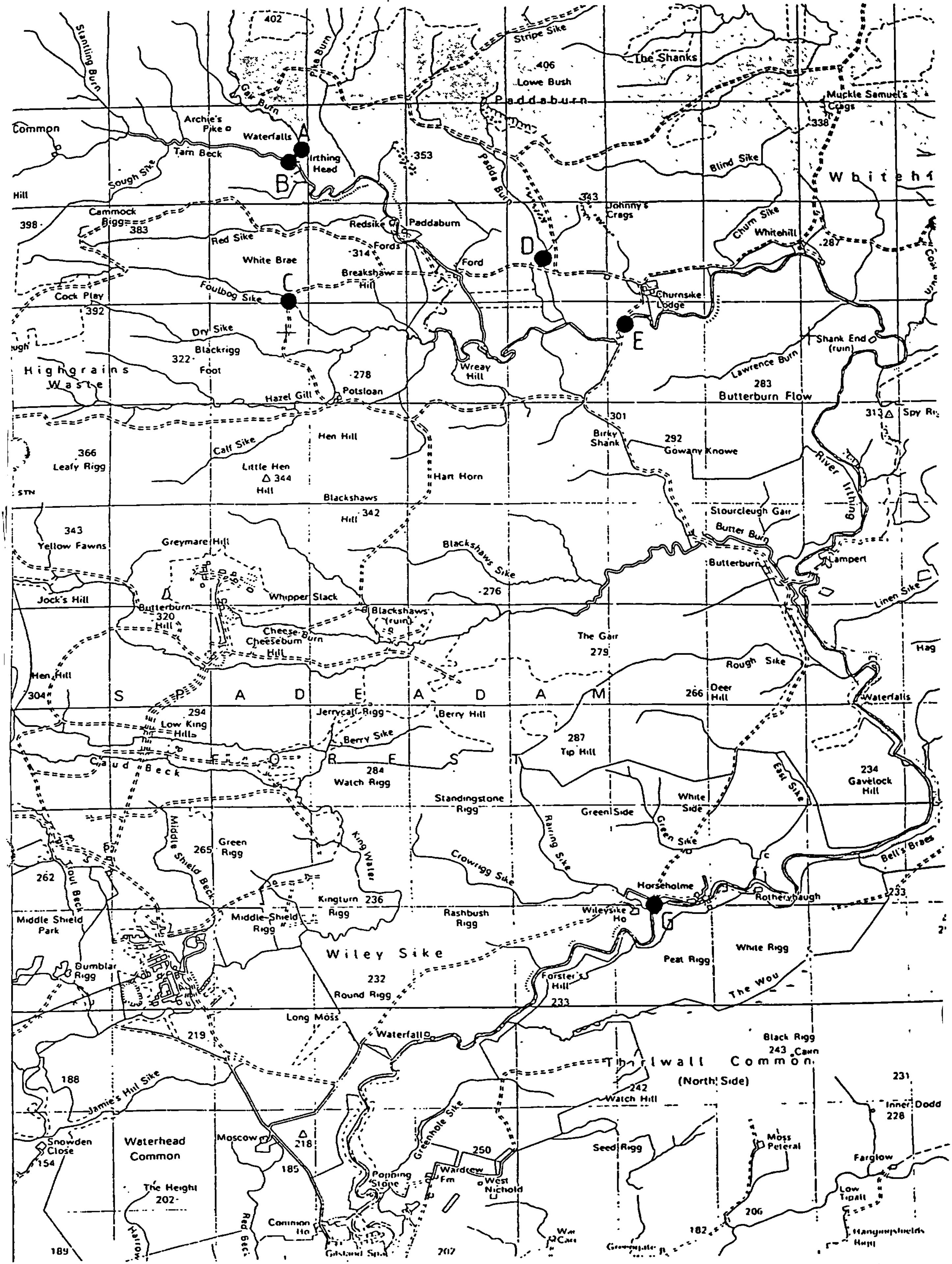
LOCATION OF SITES WITH INVERTEBRATE SAMPLING REFERRED TO IN TEXT



Key:
A Gair Burn
B Tarn Beck
C Foulbog Sike
D Padda Burn
E Irthing near Churnsike
F Coal Burn
G Irthing near Wileysike

APPENDIX 1

ELECTRIC FISHING SURVEY RESULTS
SITE - COAL BURN 100m U.S. GAUGING STATION
DATE - 04-11-93
LENGTH FISHED 67 m.   MEAN WIDTH 1.02 m.   AREA FISHED 68.3 square m.

FISH	CATCH 1	CATCH 2	CATCH 3	TOTAL	ESTIMATE	EFFICIENCY	CONFIDENCE LIMITS
trout 0+	1	0	0	1	1		
trout 1++	8	6	1	15	17	53%	17 +/- 5

COMMENTS :
Re. trout 0+ - total catch taken in first fishing

DENSITY (area)

	NUMERICAL DENSITY - fish/sq. m.	CRUDE BIOMASS DENSITY - gms/sq. m.
trout 0+	0.015	0.03
trout 1++	0.249	6.28
Salmonid (total)	0.264	6.31

DENSITY (linear)

	NUMERICAL DENSITY - fish/metre	CRUDE BIOMASS DENSITY - gms/metre
trout 0+	0.015	0.03
trout 1++	0.254	6.40
Salmonid (total)	0.269	6.43

SUMMARY FISH LENGTH DATA

	RANGE	MEAN	STANDARD DEVIATION	n
trout 1++	94 - 206	125.9	35.5	15

Coalburn invertebrate kick samples 4.11.93

SPECIES LISTING FOR SELECTED INVERTEBRATE SAMPLES

SITE NO.	290	290
decimal	51	52
METHOD	1	1
YEAR	93	93
MONTH	11	11
DAY	04	04
Taeniopteryx nebulosa	2	2
Protonemura sp		1
Protonemura meyeri	2	3
Amphinemura sulcicollis	2	2
Nemoura avicularis		2
Leuctra hippopus	2	4
Leuctra nigra	1	
Perlodes microcephala	1	1
Isoperla grammatica	3	3
Chloroperla torrentium	1	
Paraleptophlebia submarginata	2	2
Rhyacophila dorsalis	2	1
Plectrocnemia conspersa	2	2
Polycentropus flavomaculatus	2	
Limnephilidae	2	2
Silo pallipes		1
Hydraena sp	2	2
Helodidae	1	2
Elmis aenea	3	4
Limnius volckmari	2	2
Oulimnius sp	4	3
Tipulidae	1	
Pedicia rivosa		2
Dicranota sp	2	2
Chironomidae	2	2
Simuliidae	2	2
Empididae	1	1
Collembola	2	2
Tubificidae	1	
Erpobdella octoculata		1
TOTAL TAXA	25	25
TRENT BIOTIC INDEX	11	11
CDC INDEX		
BMWP SCORE	106	108
ASPT VALUE	6.63	6.75
INFERRED NWC CLASS		

Key to site numbers listed above

290.51	NY695779	Coal Burn 170m U.S. guaging station
290.52	NY694778	Coal Burn 100m U.S. guaging station

KEY : Relative abundance figures in body of the table -
1=1 specimen in sample, 2=2-5 specimens, 3=6-20 specimens, 4=21-100 specimens, 5=101-500 specimens, 6=500+ specimens

APPENDIX 3

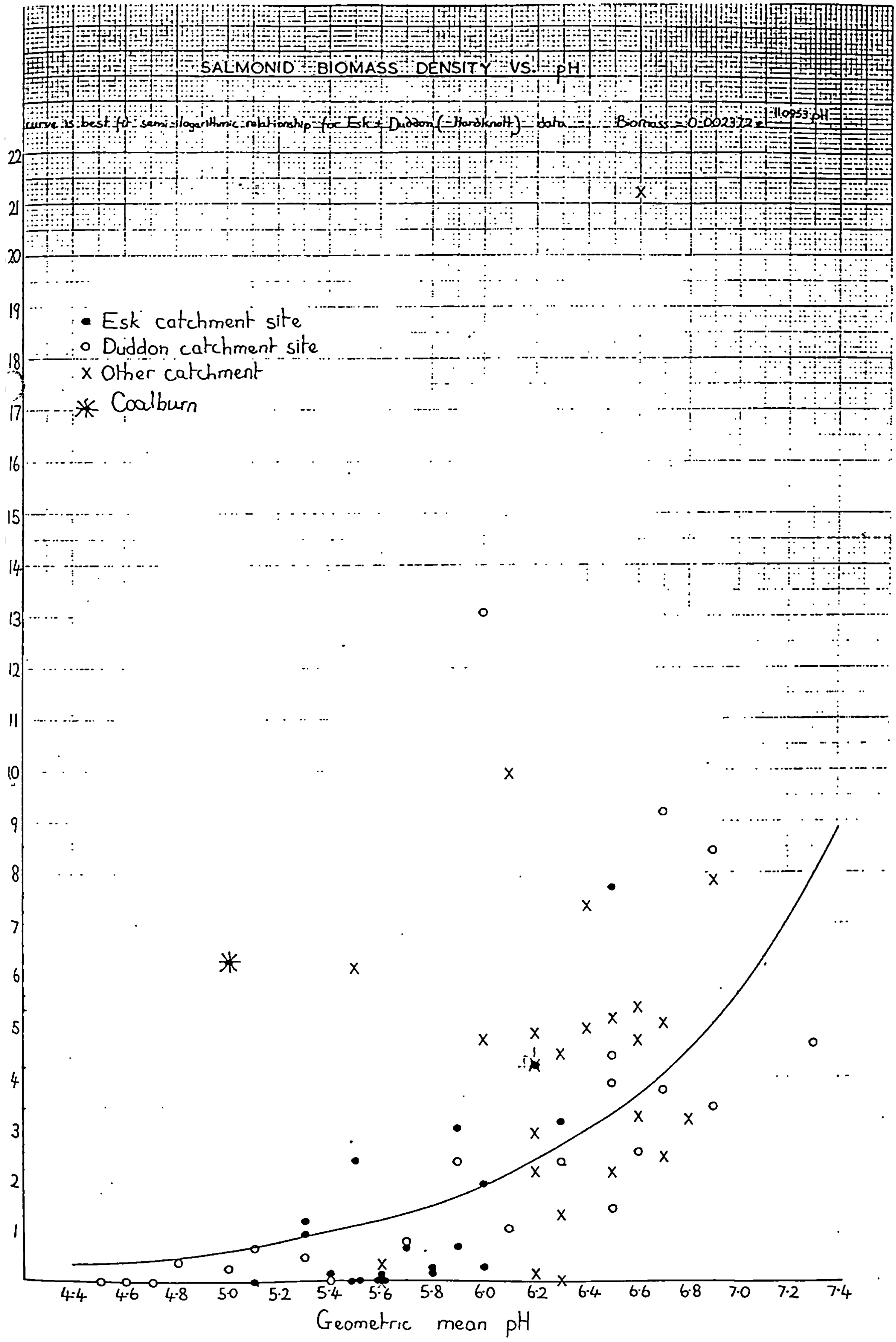
Ranking of a selection of salmonid nursery (type) stream sites in N.W. Northern Area based on total 1+ and older Salmonid density estimates

Beck	Catchment	Ref	Fish/m^2
Melmerby Beck (a)	Eden	9	1.96
Whinlatter Gill	Cocker	7	1.83
Melmerby Beck (b)	Eden	9	1.19
Hardknott Gill	Duddon	7	1.07
Aiken Beck	Cocker	9	.84
Troutbeck	Greta	9	.75
Glenderaterra Beck	Greta	7	.75
Raven Beck	Eden	9	.73
Black Beck	Ehen	9	.72
Whinlatter Gill	Cocker	9	.60
Mere Beck	Esk	7	.51
Mere Beck	Esk	7*	.48
Hollins Beck	Ehen	1	.45
Kirk Beck (a)	Ehen	1	.43
Black Burn	Liddle	8	.42
Aiken Beck	Cocker	7	.42
Greendale Beck	Irt	7	.42
Tinnis Burn	Liddle	8	.42
Newlands Beck	Derwent	7	.41
Black Beck	Ehen	1	.40
Grainsgill Beck (a)	Caldew	4	.40
Logan Beck	Duddon	7	.38
Smithy Beck	Ehen	7	.38
River Bleng	Bleng	7	.38
Sparrishaw Beck (e)	Bela	5	.38
Latterbarrow Beck	Esk	7	.36
Sparrishaw Beck (d)	Bela	5	.35
Sparrishaw Beck (b)	Bela	5	.33
Worm Gill	Calder	7	.33
Grainsgill Beck (b)	Caldew	4	.32
Croasdale Beck (b)	Ehen	1	.30
Eel Beck	Esk	7*	.28
Muir Burn	Liddle	8	.27
Raise Beck	Rothay	7	.27
Sparrishaw Beck (b)	Bela	5	.26
Mere Beck	Ehen	1	.26
Blea Beck	Duddon	7	.26
Dacre Beck	Eamont	2	.25
Mosedale Beck	Greta	6	.25
Holehouse Gill	Duddon	7	.25
Fisher Beck	Esk	7*	.25
Sparrishaw Beck (f)	Bela	5	.25
Keskadale Beck	Derwent	7	.25
Croasdale Beck (c)	Ehen	1	.24
Parkend Beck	Caldew	3	.23
Thackthwaite Beck	Eamont	2	.23
Croasdale Beck (a)	Ehen	1	.23
Kirk Beck (b)	Ehen	1	.23
Sparrishaw Beck (c)	Bela	5	.23
Skitwath Beck	Eamont	2	.22
Rowland Beck (a)	Ehen	1	.21
Rowland Beck (b)	Ehen	1	.21
Fall Beck (b)	Bela	5	.21
Gobling Beck	Duddon	7	.21
Lingmell Beck	Irt	7	.20
Sparrishaw Beck (a)	Bela	5	.20
Troutbeck	Greta	6	.20
Helm Beck	Eden	9	.20

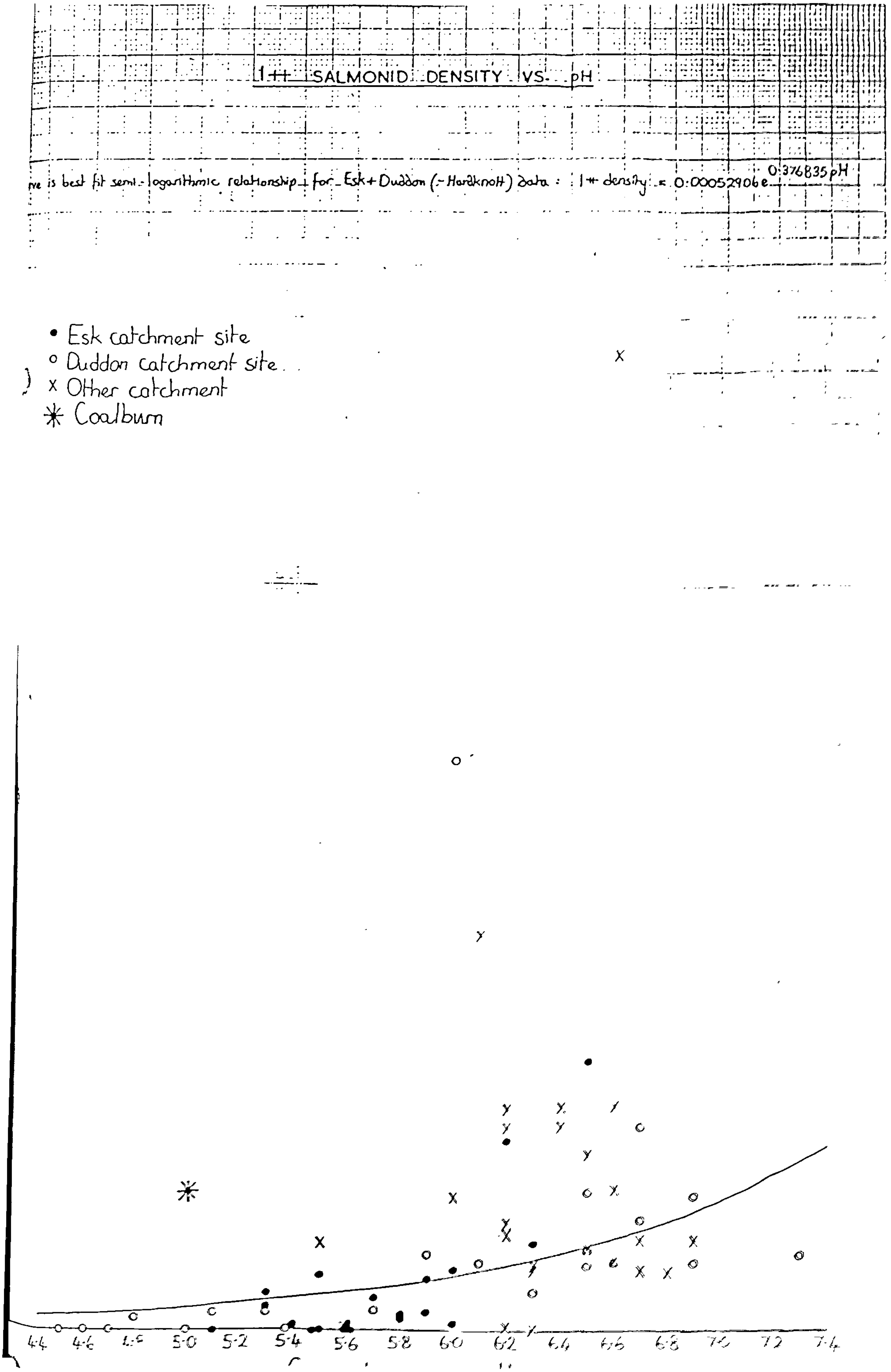
APPENDIX 3
continued

Beck	Catchment	Ref	Fish/m^2
Old Petteril	Petteril	5	.18
Stonethwaite Beck	Derwent	7	.18
Byre Burn	Border Esk	9	.17
Bannerdale Beck	Eamont	7	.17
Borrow Beck	Lune	7	.17
River Brathay	Brathay	7	.17
Birker Beck	Esk	7	.17
Fall Beck (a)	Bela	5	.17
River Calder	Calder	7	.16
St. Johns Beck	Greta	6	.15
Old Park Beck	Duddon	7	.15
Grassguards Gill	Duddon	7	.15
Dub Beck (b)	Keekle	1	.14
Cooper Beck	Eamont	2	.14
Hollow Moss Beck	Duddon	7	.14
Smithy Beck	Ehen	9	.14
Sling Beck	Duddon	7	.13
Crosby Gill	Duddon	7	.13
Cockley Beck	Duddon	7	.13
Aira Beck	Eamont	7	.13
Grainsgill Beck (c)	Caldew	4	.12
Sparrishaw Beck (d)	Bela	5	.12
River Mite	Mite	7	.12
Tarn Beck (ptc Gobling)	Duddon	7	.12
Kershope Burn	Liddle	8	.12
Hardknott Gill	Esk	7	.12
Troutbeck	Leven	7	.11
Mosedale Beck	Irt	7	.11
Swindale Beck	Lowther	7	.11
Waterside Beck	Ehen	1	.11
Black Beck (b)	Ehen	1	.10
Blackdyke Beck	Eamont	2	.10
Lin Beck	Esk	7	.10
Latterbarrow Beck	Esk	7*	.10
Fisher Beck	Esk	7	.10
Lin Beck	Esk	7*	.09
Hardknott Gill	Esk	7*	.09
Old Petteril (b)	Petteril	5	.07
Dodknott Gill	Esk	7	.06
Dub Beck (a)	Keekle	1	.06
Birker Beck	Esk	7*	.06
Blea Beck	Esk	7	.04
The Syke	Duddon	7	.04
Whillan Beck	Esk	7	.03
Dodknott Gill	Esk	7*	.03
Blea Beck	Esk	7*	.02
Moasdale Beck	Duddon	7	.02
Whillan Beck	Esk	7*	.02
R. Liza	Ehen	7	.01
Derwent (Seathwaite)	Derwent	7	.01
trib d/s Spothow	Esk	7	.01
Spothow Gill	Esk	7*	0
Spothow Gill	Esk	7	0
trib d/s Spothow	Esk	7*	0
Esk (Great Moss)	Esk	7*	0
Esk (Great Moss)	Esk	7	0
Lingcove Beck	Esk	7*	0
Lingcove Beck	Esk	7	0
Blea Beck	Lune	7	0
Gt. Langdale Beck	Brathay	7	0
Tarn Beck (Tongue H.)	Duddon	7	0
[illegible]	Duddon	7	0

Coalburn fish population and pH in relation to studies on Lake District acid streams

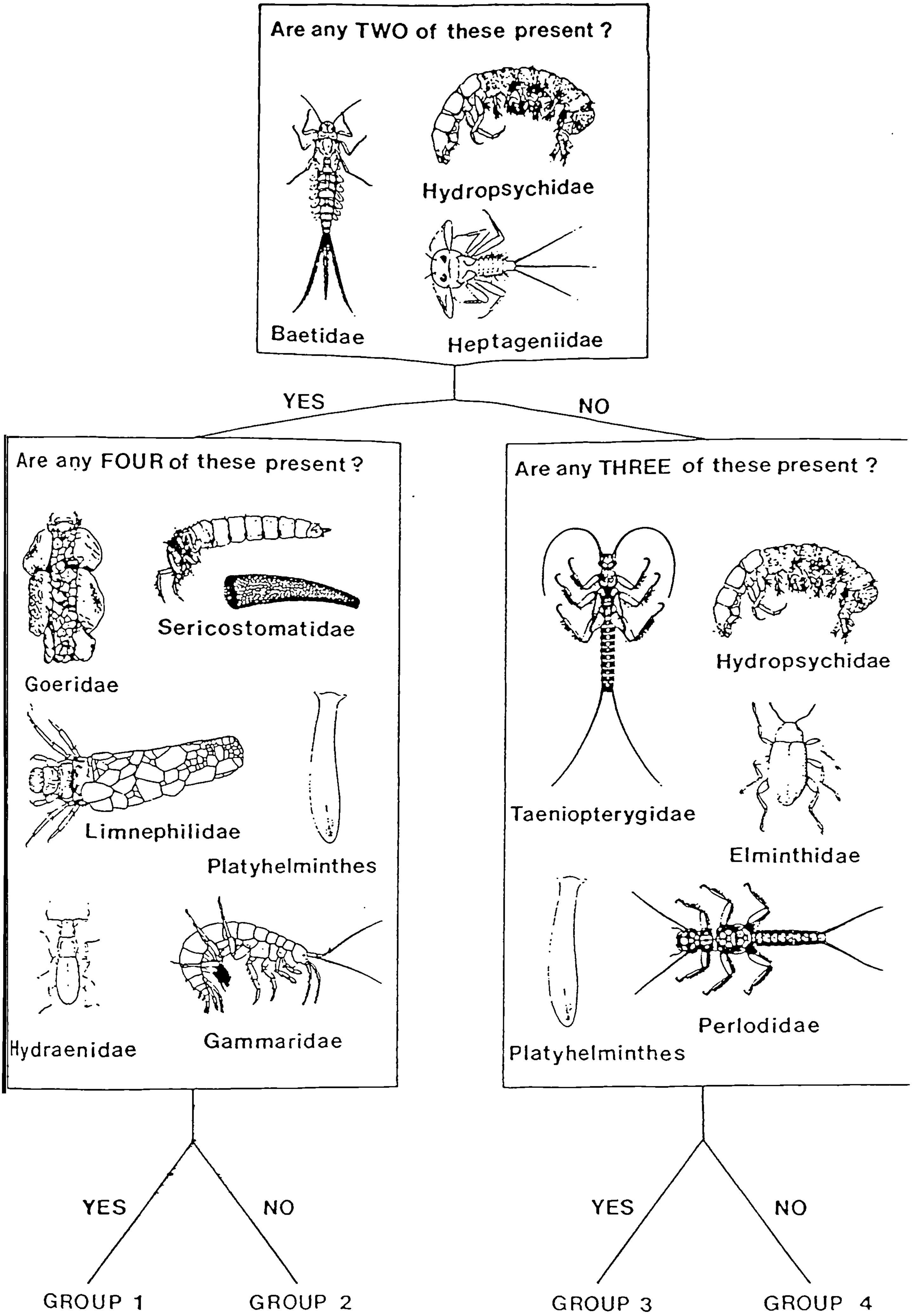


Coalburn fish population and pH in relation to studies on Lake District acid streams



APPENDIX 5

Macro-invertebrate indicator system for detection of acidic conditions in upland British streams (Rutt et al)

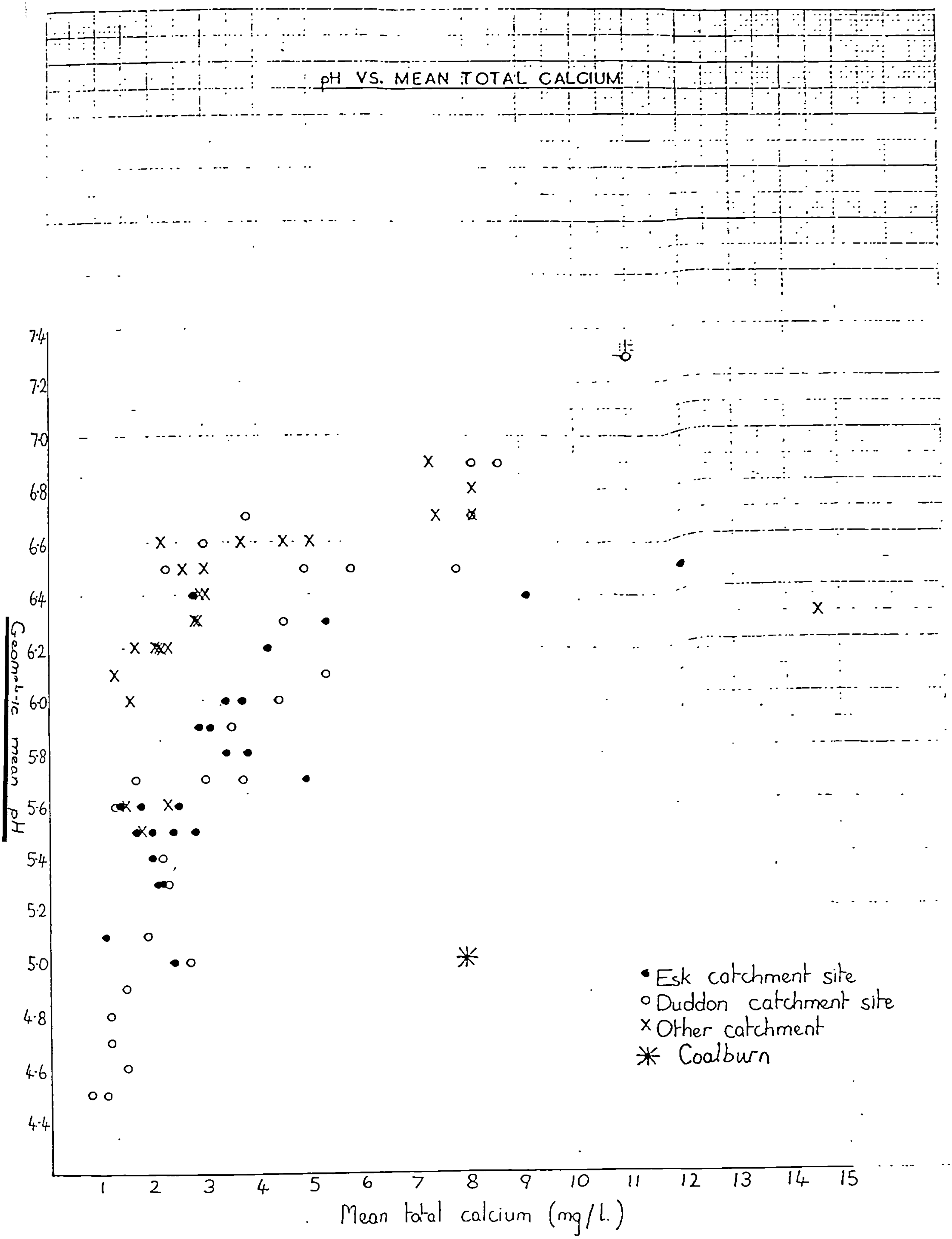


Stream groups identified by indicator key (Rutt et al)

Table 1 Characteristics of the stream groups.

Stream Group	Characteristics (all values are annual means)
1	Non-acidic streams, generally of small catchment area (< 10 km^2). 83 % have pH > 6.0, 100 % have pH > 5.5. 75 % of streams have a filterable aluminium concentration < 50 µg l^{-1}, 93 % < 100 µg l^{-1}. In general moderately well-buffered: 80 % have total hardness > 10 mg l^{-1}. Diverse fauna.
2	Non-acidic streams, generally with catchment area > 10 km^2. 91 % with pH > 6.0, 97 % with pH > 5.5. 90 % of streams have filterable aluminium < 100 µg l^{-1}. Variable buffering capacity: 69 % with total hardness > 10 mg l^{-1}. Fairly diverse fauna.
3	Acidic streams : 71 % with pH < 6.0, 87 % with filterable aluminium > 50 ug l^{-1}, 53 % with Al > 100 µg l^{-1}. Poorly buffered : 76 % with total hardness < 10 mg l^{-1}, 95 % with hardness < 15 mg l^{-1}. Impoverished fauna. Likely to be vulnerable to enhanced acidification by conifer forestry.
4	Acidic streams : 75 % with pH < 6.0, 89 % with filterable aluminium > 50 µg l^{-1}, 78 % with Al $>$ 100 µg l^{-1}. Poorly buffered : 83 % with total hardness < 15 mg l^{-1}. Very impoverished fauna. Likely to be vulnerable to enhanced acidification by conifer forestry.

Coalburn calcium and pH in relation to studies on Lake District acid streams



Routine macro-invertebrate kick sample data from upper River Irthing sites

SELECTED SITE - River Irthing 20m D.S. bridge at Churnsike

YEAR	93	93	93	92	92	92	91	91	91	90	90	90	89	89	88	88	87	87
MONTH	09	06	03	09	07	02	10	06	03	10	08	03	11	04	06	02	06	03
DAY	03	11	12	21	06	21	14	06	14	26	24	12	23	04	27	22	05	10
Plecoptera													2					
Taeniopterygidae	2		2	3		4	2		1	2	2		2			3		
Nemouridae			4			3	2							1				
Protonemura sp									2							2		
Amphinemura sp				2		2			3	1		2		2		2	2	
Nemoura sp				3												2		
Leuctridae	3	2	4	2	2	2		2	3	2	2	1	2	2	2	3	2	3
Capnidae						3												
Perlodidae							2		2		1	2				4		
Perlodes microcephala	3		1	2												2		3
Isoperla sp		3	4	1		4		2	3			4	4	3	2		3	3
Dinocras cephalotes													1				1	
Perla bipunctata							2											
Chloroperlidae		2	2					2	2			2						2
Baetidae		3		3	3		2	2		2	4		3			2	3	
Baetis sp		1	3				2		2						2			
Baetis scambus		2																
Baetis rhodani	3	3	2	3		4		3	2	3			2	3	3	4	2	3
Baetis muticus				2		4			2	2			1				2	
Centroptilum luteolum										2								
Centroptilum pennulatum	3																	
Heptageniidae	4			5			1				3						2	
Rhithrogena semicolorata			3										2	2		4	3	
Heptagenia sp										3			1					
Ecdyonurus sp	3	3	4	4	3	4	3	3	2	2		3	4	4	3	2	3	3
Leptophlebiidae		2	2	3	2	2	2	2	2	2			1					2
Ephemerella sp	3	4			3			5		1	2				4		3	
Ephemera sp	3	4	1	3	2	2	1	1		2	2	3	2				3	
Caenidae										3		4						
Caenis sp		2	3			2		3	3				4				3	
Rhyacophila sp	1		1									2						1
Polycentropidae	2	2	1	2	2	2	3	2	1	2	2			3	2		2	1
Hydropsychidae			2	3		1	2	2	2	2	1	2	2		1	2		2
Hydroptilidae	1	2						3			2							
Limnephilidae		3	2		2	3		2		1		2			1		2	
Odontocerum albicorne	1																	
Leptoceridae	3	3	3	4	2	3	1	2	2	3	2	1						
Goeridae										3								
Lepidostomatidae			1			2		2		2								
Sericostomatidae	1	2	1	1		2	2		3	2	2	2	1					
Cased caddis indet													2					
Haliplidae		3						2			2		1		2			
Dytiscidae	3	3	2	2	2			3			3			2	2			
Gyrinidae			2				2											
Hydraena sp	3	2	3	2			1	1	2	2		1	2			1		
Elminthidae				3			2	3			2	2				2		
Elmis aenea	3	4	4	3		3	4	3	4	2	3	2		2	3	2		
Esolus sp	3				3								2				1	
Limnius volckmari	3	4	4	4		3	3	3	2	2	4	3	5	2	3	4	4	1
Oulimnius sp	3	3	4	2	1	2	2		3	2		3						
Corixidae										1								
Sialis sp			2	1	3													
Diptera indet			1	1						1								
Tipulidae													1			1		
Pedicia rivosa													2					
Dicranota sp			1	1		1	2		2	2	1		1			1	2	
Ceratopogonidae			1	2									1					
Red chironomids					2		1					1		1			1	2
Chironomidae	3	3	4	3	2	3	2	3	3	2	3	2	3		4		3	
Simuliidae		2	2			2				2		2			2	2		
Atherix ibis	2	2		2				1		1	2			2			1	
Gammarus sp																2		
Gammarus pulex	3	2	4	3	2	4	3	2	2	3	2	2	3	3	1		2	2
Hydracarina	4	4	3	4		2	4	4	2	3	4	3	3	2	3		3	
Lymnaea peregra	2	2	1	3			2					2	3	3	3			
Ancylus fluviatilis							1	1			1							
Sphaeridae	2	2		2			2		2	2								
Naididae										1								
Tubificidae		2	2	2		2						2	2			1	2	
Lumbricidae			1						1									
Glossiphonidae											1							
Theromyzon tessulatum			1															
Glossiphonia complanata						1				1		1						
Helobdella stagnalis	1	1		1														
Erpobdella octoculata		1	1	2		1		1		2	2		2					
TOTAL TAXA	28	33	39	36	16	29	28	28	27	36	25	26	31	16	18	21	24	13
TRENT BIOTIC INDEX	12	13	14	13	9	12	11	12	11	13	11	11	12	9	10	10	11	9
CDC INDEX	aa	aa	aa	aa	aa	aa	aa	aa	aa	ab	aa	aa	aa	aa	aa	aa	aa	aa
BMWP SCORE	146	167	196	148	100	167	143	163	137	180	142	133	139	69	94	83	111	86
ASPT VALUE	6.95	6.42	6.53	6.17	7.14	6.96	6.81	7.09	6.85	6.67	6.76	6.65	6.62	6.27	6.27	6.38	6.94	7.17
INFERRED NWC CLASS	1A	1A	1A	1A	1A	1A	1A	1A	1A	1A	1A	1A	1A	1A	1A	1A	1A	1A

KEY : Relative abundance figures in body of the table -

[illegible] 4:21-100 specimens, 5:101-500 specimens, 6:500+ specimens

SELECTED SITE - River Irthing at Wileysike

YEAR	93	93	93	92	92	92	91	91	91	90	90	90	89	89	88	88	87	87
MONTH	09	06	03	09	07	02	10	06	03	10	07	03	11	04	06	02	06	03
DAY	03	11	12	21	06	21	14	06	14	26	16	12	23	04	27	22	05	10
Taeniopterygidae	1		3	4		3	1			2			2			2		
Nemouridae			2				2					1						1
Amphinemura sp												1						2
Leuctridae		4	3		3	4		3	2		3	2			4	3	2	
Perlodidae									3			2				2		1
Perlodes microcephala												1						
Isoperla sp		3	4			3		3	2			2	2	2			3	
Perlidae		2																
Dinocras cephalotes											2							
Perla bipunctata											1							
Chloroperlidae		2						2				1		2			2	
Baetidae					3							2	2					
Baetis sp									2		3			2	2			
Baetis scambus	3	2															2	
Baetis rhodani	4	3	5	3		5		4	3	2	4	4	2	4	3	4	3	4
Baetis muticus	2	2	3	2	2	2	2	2	1		2		2		2			
Centroptilum luteolum												2						
Heptageniidae	5			5	1		2	4		2		2		2				
Rhithrogena semicolorata	3	4	5					3				4	1	4		4	4	4
Heptagenia sp										3			2					
Ecdyonurus sp	4	3	3	4	3	3	4	3			4	4	3	4	4	2	4	3
Leptophlebiidae			2	3		4	2		4	2			1					
Ephemerella sp	3	4		1	4			5			4				4		3	
Caenidae							3			3		2						
Caenis sp	2	3	4	3	2	3		4	4		2		3	3	2		3	
Rhyacophila sp		3	2	1		2		1	2			2		2				
Glossosoma sp			1															
Polycentropidae	3	1	1	2		2		2	2				1		2	1	3	
Hydropsychidae	4	4	3	5		4	3	2	3	3	1	2	3	3	1	2	2	3
Hydroptilidae		2									2							
Phryganeidae																	1	
Limnephilidae		1	1	2									1					
Sericostomatidae												1						
Cased caddis indet																	1	
Coleoptera indet															2		1	
Dytiscidae		1		1														
Hydrophilidae									1									
Hydraena sp	1	1		2		1							1	1				
Elminthidae		4		3			2				2	2						
Elmis aenea	3	2				2		2	2	2			2		2			
Esolus sp			2										4				2	2
Limnius volckmari	3	4	4	3	3	4	3	2	3	3	3	2	3	3	2	2	3	
Oulimnius sp						2			2					2				
Diptera indet				1								1						
Tipulidae							2											
Dicranota sp	2			1								2	2		2	1		
Ceratopogonidae	2	2																
Red chironomids		2						1									1	
Chironomidae	4	4	3	3	3	4	4	5	2	2	4	2	3	3	4		3	
Simuliidae	2		2					2				2						
Atherix ibis							1											
Gammarus pulex	4	3	4	4	3	4	4	3	3	3	3		2	2	2	3	2	
Hydracarina	3	2	2	3		2		2		2	3		2	2	3			
Lymnaea peregra						1							2					
Ancylus fluviatilis	1	2	1	2	1	1	2	1			1		2			1		2
Naididae		2									2							
Tubificidae	2	2	2	2		2	2		2	2	2			2				1
Lumbriculidae			2				1											
Lumbricidae				1					1	1	1		1					
Glossiphonia complanata		1		1							1							
Helobdella stagnalis	2											1						
Erpobdellidae					2													
Erpobdella octoculata	1	2	1	2		2			2	2	1		2	1				
Gordioidea		1																
TOTAL TAXA	24	32	25	26	12	22	17	21	20	15	22	24	25	18	16	12	19	10
TRENT BIOTIC INDEX	10	12	11	10	7	11	9	10	10	8	10	10	11	10	8	9	10	8
CDC INDEX	ab	aa	ab	ab	aa	ba	ab	aa	ab	ab	aa	aa	ab	ab	aa	ab	ba	aa
BMWP SCORE	94	139	122	118	63	111	78	104	82	63	88	100	106	75	71	78	109	48
ASPT VALUE	5.53	6.32	6.42	5.9	6.3	6.17	6	6.93	5.66	5.73	5.87	6.67	5.89	5.77	6.45	7.09	7.27	6
INFERRED NWC CLASS	1A	1A	1A	1A	1B	1A	1B	1A	1A	1B	1A	1A	1A	1A	1A	1B	1A	1B

KEY : Relative abundance figures in body of the table -
1:1 specimen in sample, 2:2-5 specimens, 3:6-20 specimens, 4:21-100 specimens, 5:101-500 specimens, 6:500+ specimens

APPENDIX 8

Macro-invertebrate kick sample data 1987-1990 from selected upper Irthing tributaries

SELECTED SITE - Gair Burn at NY629785

YEAR	90	89	89	88	88	87	87
MONTH	04	10	03	06	02	07	03
DAY	27	26	17	27	22	06	11
Taeniopterygidae			3		2		3
Nemouridae			2				
Protonemura sp		2			3		
Amphinemura sp	3		3		3		3
Nemoura sp							3
Leuctridae	4	2	4	3	3	3	3
Perlodidae		2			3		
Perlodes microcephala		2					1
Isoperla sp	3	3	2	2			3
Perla bipunctata		2	2		2	1	1
Chloroperlidae	3		2		2	2	
Baetidae			2		2	2	2
Baetis sp				3			
Baetis rhodani				3	2	2	2
Heptageniidae						2	
Rhithrogena semicolorata		3			2		3
Heptagenia sp		3					
Ecdyonurus sp	4	2		3	2	3	
Leptophlebiidae	2	1					
Ephemerella sp				3		2	
Caenidae	2						
Caenis sp						2	
Rhyacophila sp		1		2	1		2
Polycentropidae	3			2	1	2	
Hydropsychidae		2					
Limnephilidae					1	2	
Leptoceridae	1						
Sericostomatidae	1						2
Coleoptera indet				2			
Dytiscidae	2			2	2	2	
Hydraena sp	2	2				2	
Elminthidae				3			
Elmis aenea		2		2		2	
Esclus sp	2						
Limnius volckmari	3	1	2	2		2	2
Oulimnius sp						2	
Diptera indet				1			
Tipulidae	1						
Dicranota sp						2	
Chironomidae			2	4		3	
Simuliidae	2		2				
Hydracarina	3			3		3	
TOTAL TAXA	17	15	11	16	15	19	13
TRENT BIOTIC INDEX	10	9	6	9	9	10	9
CDC INDEX	aa	aa	aa	aa	aa	aa	[illegible]
BMWP SCORE	116	79	73	70	97	97	[illegible]
ASPT VALUE	7.73	7.9	7.3	7	6.93	6.93	[illegible]
INFERRED RAC CLASS	1A	1A	1A	1A	1A	1A	[illegible]

KEY : Relative abundance figures in body of the table -
1=1 specimen in sample, 2=2-5 specimens, 3=6-20 specimens, 4=21-100 specimens, 5=101-500 specimens, 6=500+ specim

SELECTED SITE - Tarn Beck at NY629785

YEAR	90	89	89	88	88	87	87
MONTH	04	10	03	06	02	07	03
DAY	27	26	17	27	22	06	11
Taeniopterygidae			2		2		1
Nemouridae			3				
Protonemura sp		2			2		
Amphinemura sp	2		3		3		3
Nemoura sp							2
Leuctridae	4	3	4	3	3	4	3
Perlodidae		2			3		
Perlodes microcephala		2			1		2
Isoperla sp	3	3	2			1	3
Perlidae			2				
Dinocras cephalotes	2		2				1
Perla bipunctata	2	3		3	2		
Chloroperlidae	2	2	2			2	
Siphlonuridae	1		2				
Baetidae			2		1	2	
Baetis sp				2	1		
Baetis scambus						2	
Baetis rhodani		2	3	3	3	2	
Rhithrogena semicolorata	2	3	4		4		3
Heptagenia sp		3					
Ecdyonurus sp	3	2	4	3		4	3
Leptophlebiidae	2		2		1		
Ephemerella sp				3		3	
Caenidae	2						
Caenis sp				1		3	
Rhyacophila sp	2	2	2	2		2	2
Glossosoma sp						2	
Polycentropidae	3		2	2	2	2	2
Hydropsychidae	2	2	2		1		2
Limnephilidae	1				1		
Dytiscidae	1		2		2	3	
Hydraena sp	3	2	1	2		2	
Elminthidae				2			
Elmis aenea	3	2	1	2		2	2
Esolus sp	1						
Limnius volckmari	3	2	2	2	2	3	2
Oulimnius sp		1				2	
Diptera indet			1			1	
Tipulidae					1		
Dicranota sp		2		2			
Chironomidae	2		2	2		1	
Hydracarina	2		2	2		2	
Lymnaea peregra	2	1					
Ancylus fluviatilis						1	
Lumbricidae		1				1	
TOTAL TAXA	23	20	24	18	19	22	14
TRENT BIOTIC INDEX	11	10	10	9	9	10	9
CPC INDEX	aa	aa	aa	aa	aa	aa	aa
BMWP SCORE	130	92	127	82	105	66	51
ASPT VALUE	7.22	6.57	7.47	6.83	7.5	6.6	5.1
INFERRED NWC CLASS	1A	1A	1A	1A	1A	1A	1A

KEY : Relative abundance figures in body of the table -
1=1 specimen in sample, 2=2-5 specimens, 3=6-20 specimens, 4=21-100 specimens, 5=101-500 specimens, 6=500+ specimens

SELECTED SITE - Foulbog Sike at NY628771

YEAR	90	89	89	88	88	87
MONTH	04	10	03	06	02	07
DAY	27	26	17	27	22	06
Taeniopterygidae			2		3	
Nemouridae	2					2
Protonemura sp					2	
Amphinemura sp	2		3		3	
Leuctridae	3	2	3	2	4	2
Perlodidae		2	2		4	
Isoperla sp	2		3			
Dinocras cephalotes	3	3	2	2	2	2
Chloroperlidae			3		2	2
Baetidae	2		2			2
Baetis sp				2		
Baetis scambus						2
Baetis rhodani	2		2	2	4	2
Baetis muticus		1	2			
Heptageniidae		3			1	2
Rhithrogena semicolorata	2		2		3	
Ecdyonurus sp	3		4	2	4	3
Leptophlebiidae	2	3		2		2
Ephemerella sp				3		2
Ephemera sp	1					2
Caenis sp						2
Rhyacophila sp		2	2	1	2	1
Polycentropidae	3	3	1	2		3
Hydroptilidae		2				
Limnephilidae	1					2
Odontocerum albicorne		2				
Cased caddis indet			2		2	
Coleoptera indet				3		2
Dytiscidae	3		2	2	2	3
Hydraena sp	2		1	2	2	2
Helodidae		1				
Elmis aenea		1			2	
Esolus sp	2					
Limnius volckmari	2		2		2	3
Veliidae						2
Dicranota sp		1				
Chironomidae	3	2	2	4		2
Simuliidae			2		2	
Gammarus pulex	4	3	3	2	3	2
Hydracarina	2			2		3
Planorbidae	1					
Tubificidae	1					
Lumbricidae		1	1			1
TOTAL TAXA	22	16	22	15	19	25
TRENT BIOTIC INDEX	10	11	10	9	10	11
CDC INDEX	aa	ab	aa	aa	ab	aa
BMWP SCORE	110	[illegible]	122	86	112	138
ASPT VALUE	[illegible]	6.15	6.78	[illegible]	7.47	[illegible]
INFERRED NWC CLASS	1A	1A	1A	1A	1A	1A

KEY : Relative abundance figures in body of the table -
1=1 specimen in sample, 2=2-5 specimens, 3=6-20 specimens, 4=21-100 specimens, 5=101-500 specimens, 6=500+ specimens

SELECTED SITE - Padda Burn at NY654773

YEAR	90	89	89	88	88	87	87
MONTH	04	10	03	06	02	07	03
DAY	27	26	17	27	22	06	11
Plecoptera		1					
Taeniopterygidae	5		3		5		
Nemouridae		2	0				2
Protonemura sp		3			3		
Amphinemura sp	3	3	3		3		
Nemoura sp							3
Leuctridae	4	3	4	3	3	3	2
Perlodidae			2		3		
Perlodes microcephala		2			1		
Isoperla sp	3	3	3	2			2
Chloroperlidae	3		2	3	2		2
Baetidae			2		3	2	2
Baetis sp				2			
Baetis rhodani				3		3	
Heptageniidae	2	2					
Rhithrogena semicolorata		2	2				
Heptagenia sp		3					
Ecdyonurus sp		3		3		3	
Ephemerella sp				2		2	
Rhyacophila sp	2	2	2	3	2		2
Polycentropidae	3	2		2		2	
Hydropsychidae		1					
Limnephilidae		1				2	
Sericostomatidae							2
Cased caddis indet					2		
Coleoptera indet				2		2	
Dytiscidae	2		2	2	2	3	
Hydraena sp	2		1			2	
Helodidae	1	3					
Elminthidae				3			
Elmis aenea	3	2	1		2	3	
Esolus sp						2	
Limnius volckmari	3		2		2	3	
Oulimnius sp						3	
Dicranota sp					1		
Chironomidae				4			
Simuliidae				2	2	2	
Hydracarina	2			2			
Planorbidae						1	
Lumbricidae				1		1	
TOTAL TAXA	14	17	14	16	15	17	8
TRENT BIOTIC INDEX	9	9	9	9	9	8	5
CDC INDEX	aa	aa	aa	aa	aa	ab	aa
BMWP SCORE	91	73	83	86	86	77	58
ASPT VALUE	7.56	7.3	7.55	6.62	7.17	5.92	6.24
INFERRED NWC CLASS	1A	1A	1A	1A	1A	1B	1B

KEY : Relative abundance figures in body of the table -
1=1 specimen in sample, 2=2-5 specimens, 3=6-20 specimens, 4=21-100 specimens, 5=101-500 specimens, 6=500+ specimens