IRON AND MANGANESE CYCLING IN THE STORM RUNOFF OF A SCOTTISH UPLAND CATCHMENT

Corinna Abesser[1,*], Ruth Robinson[1] and Chris Soulsby[2]

[1]Department of Geography and Geosciences, University of St Andrew, St Andrews, KY16 9AL, UK.

[2]Department of Geography and Environment, University of Aberdeen, Aberdeen, AB24 3UF, UK.

* corresponding author, present address: British Geological Survey, Maclean Building, Crowmarsh Gifford, Wallingford, OX10 8BB, UK. Tel: ++44(0)1491 692296, Fax: ++44(0) 1491 692345, E-mail: c.abesser@bgs.ac.uk

Abstract

Factor analysis and (two-component) end member mixing analysis (EMMA) were applied to high resolution stream chemistry data from three catchments to infer sources of iron and manganese-rich runoff in the catchment area and to evaluate their temporal and spatial influence on the stream water quality. The results demonstrate that flow related changes in soilwater inputs (associated with changes in flow pathways) exert a major control on stream chemistry during storm events and depend on the soil distribution in the catchments as well as on antecedent conditions and storm intensity. Two Fe and Mn sources were identified: (1) an organic soilwater source, associated with Fe and Mn accumulation in the organic-rich upper soil horizons and (2) a deep soilwater/groundwater source arising from reduced metal mobilisation in the deeper soils. While (1) provides the dominant inputs during storm events, (2) becomes important just before peak flow when riparian groundwater is displaced into the stream giving rise to total Fe and Mn concentrations of up to 1160 µg l^{-1} and 121 µg l^{-1}, respectively. The timing of such high Fe and Mn loadings in the stream runoff has important implications for the water supply management of the catchment. Subsequent effects on lakes/ reservoirs, for example, must be considered when assigning load limits or load reduction goals for the purpose of improving/ maintaining water quality but also when planning maintenance work on the reservoir. However, a better understanding of the nature of these Fe and Mn sources is required to better (quantitatively) predict when and where undesirable Fe and Mn concentrations will occur.

Keywords: Hydrology, iron, manganese, factor analysis, EMMA, Scotland.

1 Introduction

Upland areas constitute an important component of the natural heritage of Scotland and provide the headwaters of many major river systems. As such, upland catchments are the major sources of potable, industrial and agricultural water supplies, particularly in Scotland where 96% (by volume) of the public water supplies are derived from surface waters (MacDonald, 1994).

While generally regarded as relatively undisturbed natural environments, increasing environmental pressures on upland water quality arise from acidification through sulphur and nitrogen deposition (Kirchner and Lydersen, 1995; Neal et al., 1998), high sediment loads from forestry and overgrazing (Carling et al., 2001) and mobilisation of colour and metals (Mitchell and McDonald, 1995). This has provided a major impetus for water quality research in the UK during the last few decades. Much research has been undertaken in upland catchments in Wales (Neal et al., 1997a) and North-east Scotland (Soulsby et al., 1998; 2003) and the results have significantly improved the understanding of the water quality functioning in such upland environments (Langan et al., 2001; Neal et al., 2004).

While iron (Fe) and manganese (Mn) have been included in many of these studies on upland catchment hydrogeochemistry (Reid et al., 1981; Giusti and Neal, 1993; Heal, 2001), the main research focus has been on the impact of acid deposition and aluminium mobilisation. Comparatively little work has been dedicated to water quality problems related to the occurrence of background high loadings of Fe and Mn, probably because of their, generally, less harmful effect compared to inorganic aluminium species. However, at high concentrations, Mn toxicity to fish (Nyberg et al., 1995) and humans (Kondakis et al., 1989) has been suggested, and high Fe levels can also have ecological impacts, such as destruction of fish spawning grounds (Marsden and Mackay, 2001) and smothering of benthos with iron hydroxides (Younger, 2001). Moreover, the increased presence of Fe and Mn in stream runoff and water bodies is of growing concern to many water authorities in the UK (Little and McFadzean, 1991; Schofield et al., 1991; Graham et al., 2002) and the EC Drinking Water Directive (CEC Commission of European Communities, 1980) has set the mandatory maximum admissible concentration of Mn and Fe in drinking water at 50 $\mu g\ l^{-1}$ and 200 $\mu g\ l^{-1}$, respectively. Although only about one per cent of the drinking water samples tested across Scotland in 1996 failed to meet these EC

Standards for Mn, the majority of failures occurred in upland terrains (Heal, 2001). Temporary deterioration in Mn quality, for example, has occurred in the raw waters of Loch Bradan, south-west Scotland (Little and McFadzean, 1991), and Fe and Mn problems were also experienced in the Megget Reservoir during an excessive draw down of the water level in 1997/98 (Abesser, 2003).

Elevated Mn and Fe concentrations in streams and water bodies are commonly observed in upland regions and have been reported in a number of studies in Scotland (Reid et al., 1981; Giusti and Neal, 1993; Gavin et al., 2001), Northern England (Stunell and Younger, 1995) and Wales (Neal et al., 1997a). The high Mn and Fe concentrations are generally associated with the acidic pH and the organic nature of the poorly-drained peaty upland soils, which favour mobilisation of Mn and Fe. However, relatively little is known about the mechanisms and pathways by which these elements are delivered to streams.

Catchment hydrology is a dominant control on stream water quality and metal loading, and long-term monitoring of individual streams and catchments has been invaluable in understanding the complexity of the underlying hydrological processes. However, the majority of these studies have relied on weekly to monthly sampling regimes and spot sampling at such large intervals tends to overlook peak values and details of changes in stream chemistry during events (Peters, 1994; Jarvie et al., 2001), which are often rapid, due to the ‘flashy’ runoff response characteristic of most upland catchments. Large changes in flow and associated chemistry can occur in a matter of hours or minutes (Foster et al., 1997) and are often associated with high loadings in colour (TOC), Fe and Mn (Reid et al., 1981; Giusti and Neal, 1993; Neal et al., 1997a; Heal et al., 2002). Hence, sample collection at time scales that more closely correspond to the hydrological dynamics of the system is essential in documenting the main chemical effects associated with the rapid stream response to events and is also important for capturing the entire range of stream chemical loadings (Kirchner et al., 2004). Short-term intensive sampling during storms thereby provides insight into the hydrochemical response of individual streams/catchments to changing hydrological conditions and this allows identification of critical periods of acidic runoff and/or high metal (e.g., Fe, Mn) loading. This knowledge is essential for effective water quality management in upland catchments (Heal et al., 2002) and also for the development of future protection, management and operation strategies for increasingly vulnerable upland water supply bodies.

In this paper, high-frequency storm event data are used to assess the range of Fe and Mn loadings in three streams in the Megget catchment of Scotland and to examine the contribution of different hydrological source areas to runoff and metal loading during storm events. The approach incorporates the relatively simple technique of End Member Mixing Analysis (EMMA) in combination with the statistical techniques of R- and Q-factor analysis in order to identify the potential source areas of stream runoff at different flows (Christophersen and Hooper, 1992; Brown et al., 1999). This paper investigates stream chemical changes at high temporal resolutions in order to gain a better understanding of the underlying mechanisms of runoff generation in the Megget catchment during storm events and thus, identify the sources of Fe and Mn in the catchment area, and evaluate their temporal and spatial influence on the streamwater quality.

2 Study area

The Megget catchment is located in the Southern Uplands in the UK, about 50 km south of Edinburgh (NGR 319 622) and forms the headwaters of the Tweed catchment whose water resources have been exploited significantly (Robson et al., 1996). The Megget catchment covers an area of about 45 km^2 with altitudes ranging between 330 m and 847 m above sea level. It is an important source of drinking water and holds one of Scottish Water's largest supply reservoirs (Figure 1). The reservoir is fed by six main tributaries; Megget Burn, Winterhope Burn, Shielhope Burn, Craigierig Burn, Cramalt Burn and Linghope Burn.

Temperatures in the catchment area range between –10°C and 27°C (average annual minima and maxima measured at the Megget Dam) and mean annual rainfall in the catchment area is 1524 mm with the higher rainfall in autumn and winter. Potential evapotranspiration in the area is about 230 mm at 300 m altitude, but declines with increasing altitude (Bown and Shipley, 1982).

The underlying geology is dominated by Silurian greywackes, siltstones and shales that have been intensively folded during the Grampian Orogeny. The solid geology is covered by glacial deposits. Postglacial peat deposits occupy most of the hilltops in the catchment area while moraines and boulder clay (till) predominate on the lower ground.

The soils in the catchment are typical of upland areas. On the soliflucted stony drift and on the stabilised scree of the lower slopes, brown forest soils, rankers and podzols have developed. Peaty podzols, which are the most abundant soil type in the catchment, predominate the mid and upper slopes while blanket peat of 0.5–

1 m thickness covers much of the high ground in the area (Bown and Shipley, 1982). Peaty gleys have developed locally on boulder clay and clayey till deposits, but also at valley bottom locations where downslope drainage from the valley sides has promoted saturated, waterlogged conditions.

Low bedrock permeability and shallow soils together with the steep slopes (median slope angle 32.6°) result in a relatively flashy hydrological runoff regime although lag times between peak of rainfall and runoff peak of around nine hours have been observed for the largest stream - the Megget Burn (Grzybowski, 2001). Groundwater storage and transport in the area are mostly confined to the shallow, weathered zone (Lawrie and MacGregor, 1946; Robins, 1990) and to the superficial glacial and post-glacial deposits (Robins, 2002). Peat soils and mire systems can also hold significant quantities of water (Bragg, 2002) and in the Megget catchment, probably provide small but perennial baseflow for local springs and small streams from the peat areas.

Sheep farming is the dominant agricultural activity in the area and is concentrated in the lower reaches of the catchment. Semi-natural moorland and grassland communities form the dominant vegetation of the steep hill slopes. Small patches of coniferous forest are located along the north side of the reservoir.

3 Methodology

3.1 Data collection

Event-based sampling was carried out over a two-week period in October 2000. Water samples were collected from three streams – Shielhope Burn and Winterhope Burn, which are direct inflows to the Megget Reservoir and Peaty Muckle Burn, a second order stream within the Winterhope catchment. Streams of differing catchment size, catchment characteristics and soil type distribution were selected (see Table 1) so that the effects of these factors on stream chemistry and runoff response could also be considered.

Two automatic samplers (American Sigma Portable Wastewater Sampler) were available and allowed sampling over a 24h period at two streams simultaneously. Initially, the two automatic samplers were installed at Winterhope Burn and Shielhope Burn, where samples were collected at 2 to 4 hourly intervals, depending on the hydrological conditions. Onset and duration of each automated sampling cycle were predetermined by the sampling programme and every effort was made to coincide the removal of the full sample bottles with the end of the automated sampling cycle to keep the equipment running continuously and to cover as many storm hydrographs as possible. At Peaty Muckle Burn, samples were collected manually and up to four times a day during rainfall events and once a day during dry periods. Limited accessibility and the risk of flooding at the Shielhope site, however, required the site to be abandoned and the sampler was then moved to Peaty Muckle Burn. Details of sampling frequencies and rainstorm coverage for each site are summarised in Figure 2.

After collection, samples were transferred into clean 1-l polyethylene bottles (for general chemistry) and into 250-ml polyethylene bottles (for metal analysis). Samples collected for metal analysis were then acidified to 0.1-%vv with AristaR grade nitric acid. Immediate preservation of the unfiltered sample had the advantage that processes of precipitation and adsorption were reduced, but this meant that after filtration (in the lab) the acid available metal fraction (AA) was determined, rather than the more commonly determined colloidal/dissolved metal fraction.

All samples were delivered to the laboratory as soon as possible after collection. Sample containers were kept cool (8ºC) and in the dark and turn around times between sample collection and delivery to the laboratory did not exceed 3 days.

A suite of analysis was performed on the samples including pH, colour, alkalinity, conductivity (SEC), turbidity, major ions (Mg, Ca, SO_4), acid available and total metals (Al, Fe, Mn) and SiO_2. Chemical analysis was carried out by the Scottish Water (former East of Scotland Water) laboratory in Edinburgh using standard water-analysis techniques as follows: alkalinity was derived by titrating the sample to an end-point of pH 4.5 using a Radiometer Auto Titrator. Measurements of colour, conductivity, pH and turbidity were determined by an automated Anachem Aqualyser System. Concentrations of major and minor metallic elements and silica were measured by Inductively Coupled Plasma Optical Emission Spectrometry.

Hydrological monitoring was carried out at the sampling site at Winterhope Burn, where a pressure transducer and automatic depth level recorder (ISODAQ Systems Limited) were installed in a stilling well and stream stage was recorded at 30-minute intervals. Stream discharge was then estimated from the continuous stage recording using a stage-discharge rating curve determined in a separate study (Grzybowski, 2001). For the ungauged streams, discharge was estimated from the gauged flows at Winterhope Burn weighted by catchment area and using a simple catchment area to stream flow ratio. Although discharge at individual streams was clearly overestimated by the method, the general runoff trends were well captured (Abesser, 2003), and since relative changes are the important factor in the current application rather than absolute values, these simple discharge calculations were found to be sufficient for the purpose of this study.

Rainfall data were collected at the Megget Dam and were also made available from the Scottish Environment Protection Agency's (SEPA) automatic rain gauge at the Gordon Arms Hotel (NGR 330788 624901, altitude 228.9 m), about nine kilometres east of the Megget catchment.

3.2 **Q- and R-factor analysis**

Factor analysis is a widely used multivariate method of data reduction and has been applied in various geochemical studies where it offers a useful means for exploration of multivariate relationships within suitable data sets (Jöreskog et al., 1976; Reid et al., 1981; Davis, 1986; Walden and Smith, 1995; Heal et al., 2002). It comprises a number of related computational procedures designed for the analysis of inter-relationships within a set of variables or samples. Its prime objective is to reduce the dimensionality of the original data by looking for underlying trends inherent in the data. It transforms the original variables (or samples) into a smaller set of mutually uncorrelated 'factors', which contain the essential information of the original set of variables (or samples) and form the 'new (reduced) dimensions' of the data space.

In this study, simultaneous R- and Q-mode factor analysis was performed for each stream using the log-normalised and standardised data. Normalisation and standardisation procedures were applied in order to improve the interpretability of the results and to remove the effects of variables being measured in different scales (e.g., pH, mg l^{-1}, µg l^{-1}, mmol Eq l^{-1}). The analysis was carried out in Minitab following a procedure proposed by Walden and Smith (1995) and is detailed in Abesser (2003). The *R-mode technique* adopted for the analysis presents a principal component approach to factor analysis and as noted by Davis (1986) does not produce a 'true' factor solution. Thus, strictly speaking, the technique is not a statistical procedure but more a mathematical manipulation. Given an original (standardised) data matrix of *n* samples by *m* variables the data are first transformed into an *m x m* correlation matrix from which the eigenvalues and eigenvectors, defining how the data points are geometrically arranged in space relatively to each other, are extracted. The factors are then derived from scaled eigenvectors whose lengths are proportional to the amount of total variance. The resulting factor matrix contains 'factor loadings' for each original variable on each of the new factors. Factor loading size is therefore related to the amount of variance contributed by a variable to a particular factor. The *Q-mode technique* applied in this study follows a procedure similar to principle co-ordinates analysis (Davis, 1986; Kovach, 1995). Starting from the same standardised data set of *n* samples and *m* variables, an *n x n* similarity matrix is constructed, representing the similarities between sample pairs in terms of the way they respond to all variables. Factors are then extracted from the data using the same procedure applied in R-mode analysis and producing a factor matrix of all sample factor loadings. This time, the size of the resulting factor loading is related to the amount of variance contributed by a sample to a particular factor.

The full stream data set was used for the analysis, although for Fe, Mn and Al, only the total concentrations were included in the analysis in order to minimise effects of data redundancy and to facilitate the interpretation of the results.

3.3 End-member mixing analysis

End-Member Mixing Analysis (EMMA) is often used as a diagnostic tool to explore the importance of conceptual hydrological pathways in a given catchment area based on the observed stream chemistry. The technique is powerful in its simplicity and has been successfully applied as a hydrograph separation technique (Robson and Neal, 1990; Brown et al., 1999; Soulsby et al., 2003) using a time series of stream chemistry data and estimates and/or measurements of the end-member chemistries. The application of the approach is based on a number of assumptions (Abesser, 2003) which greatly simplify the existing complex environmental system and its validity has rightly been challenged (Kendall et al., 1995). Careful consideration of how applicable these assumptions are to the intended application is essential and this has been recognised and highlighted by the originators of EMMA (Christophersen and Neal, 1990; Neal et al., 1997b).

The main difficulty in EMMA arises from the identification of viable end-members. For the purpose of this modelling effort, a simple two-component flow model was deemed appropriate in view of the hydrochemical response observed at the streams. Alkalinity was used as the conservative tracer (Wade et al., 1999; Soulsby et al., 2003) for establishing the hydrograph split (geographic source separation) according to the classical two-component mixing model:

$$Q_{streamwater} \cdot Alk_{streamwater} = Q_{groundwater} \cdot Alk_{groundwater} + Q_{soilwater} \cdot Alk_{soilwater} \quad \text{(Eq 1)}$$

$$Q_{groundwater} + Q_{soilwater} = Q_{streamwater} \quad \text{(Eq 2)}$$

where Alk is the alkalinity, Q is discharge and the subscripts *streamwater*, *groundwater* and *soilwater* refer to those specified sources. Since alkalinity values in all streams are always positive, the conversion to Acid Neutralisation Capacity (ANC), which is strictly a more conservative measure (Neal, 2001), did not appear necessary. By combining (Eq 1) and (Eq 2), the proportion of groundwater ($\%_{gw}$) was determined from

$$\%_{gw} = 100 \cdot (Alk_{soilwater} - Alk_{streamwater} / Alk_{soilwater} - Alk_{groundwater}) \qquad (Eq\ 3)$$

and the stream water time series for the three sites were constructed using recorded and modelled flow data.

In this study, no direct measurements of groundwater or soilwater chemistry were available. Thus, the alkalinity of the groundwater end-member ($Alk_{groundwater}$) was inferred from the three lowest flow samples, collected during summer low flow, at each particular stream (Figure 3, Table 2). For the definition of the soilwater end-member ($Alk_{soilwater}$), end-member alkalinities were inferred from literature soil data (Table 2) collected from sites with similar soil types and catchment characteristics. Two models were produced assuming the soil end-member alkalinity to lie in the range between peat soils and peaty podzols and these two extremes (lowest and highest alkalinity value) were also used to assess the effect of the uncertainty in the soilwater end-member on the hydrograph separation.

4 Results

4.1 Event Chronology

There were six rainfall events during the sampling period (see Figure 2), which varied in length and magnitude, including one of the largest events of the year. Two large events occurred on 22-23 October and 24-25 October with a total rainfall of 24.8 mm and 28.2 mm and a maximum rainfall intensity of 8.0 mm h^{-1}, causing stream flow to increase by a factor of 7 and 5, respectively. Smaller events occurred on 17-18 October (4.4 mm; 1.6 mm h^{-1}), 20 October (2.4 mm; 2.4 mm h^{-1}), 27 October (3.4 mm; 0.8mm h^{-1}) and 28 October (12.8 mm; 20 mm h^{-1}). Although changes in stream flow were less dramatic in these small events, significant changes in stream chemistry were observed. As the catchment wetness increased with successive events, the stream discharge gradually increased, and stream water levels in-between rainstorm events remained higher than those at the beginning of the sampling period.

4.2 General pattern of stream response during storm events

Water composition in all streams is dominated by the dynamic response to individual storm events, characterised by the depression of pH, conductivity, alkalinity and base cations (Ca, Mg) concentrations and the dramatic rise in colour (organic matter) and metal concentrations (Figure 4 and Figure 5). The inverse relationship between weathering-related determinants (Ca, alkalinity, pH) and flow is evident in Figure 6 and is consistent with the dilution of base-rich groundwater sources with more acidic inputs from shallow, organic-rich soil horizons during storm periods. The single straight linear (positive) relationship between Ca and alkalinity indicates a similar flow-related behaviour of the weathering-derived components in all streams and suggests two component mixing of two main water types (or end-members), one corresponding to typical stormflow waters (low Ca and alkalinity) and another representing baseflow chemistry (high Ca, alkalinity). Determinants associated with soilwater sources (colour, Fe, Al) are positively related with flow, but the inter-relationships of these elements show different gradients between the streams (e.g., Al versus colour) suggesting that the high flow chemistries vary between the sampling locations.

4.3 R- and Q-mode factor analysis

The scatter plots (Figure 6) indicate that inter-relationships exist between some of the variables but not between others and that different patterns of runoff chemistry emerge for the individual streams. To analyse these inter-relationships between variables and comparing the respective properties of groups of samples, combined R- and Q-mode analysis was performed on the three stream data sets collected during intensive sampling. Accepting all components with eigenvalues >1 meant that two factors were selected from the R-mode analysis, each of which explains greater variance than the original standardised variables and together explain 85 % to 90 % of the variance in the original data (Table 3).

R-mode analysis – Variable factor loading

The first factor is by far the most dominant factor in all streams accounting for 67 % to 82 % of the variability. It has high loadings across all variables and divides the original variables into two distinct groups with high negative loadings on pH, alkalinity, conductivity, base cations, Si and SO_4 and high positive loadings on Al and colour, Fe and Mn (Table 3).

The high positive loadings on Al and colour reflect the strong influence of the soilwater component. Soilwater chemistry is influenced by decomposition of organic matter in the upper horizons and becomes important during rainfall events when stream runoff is derived mainly from overland flow and subsurface storm flows generated in the upper soil horizons. Soilwater also contains high amounts of organically complexed metals, represented by strong loadings on Fe, Mn and in particular Al (Table 3), which together with hydrogen (strong negative pH loadings) is the dominant cation in the solution of acidic soils and forms strong complexes with dissolved organic matter (Drever, 1997). Silica, SO_4, alkalinity and base cations are generally indicative of bedrock weathering and the high negative loadings on factor 1 are consistent with the dilution of base-rich inputs from groundwater and deeper mineral soils with more acidic soilwater sources during storm periods. Hence, factor 1 reflects the flow related changes in stream chemistry and, in this study, is interpreted as the dilution of stream baseflow with soilwater inputs that are high in Al and colour during storm events, where water from the upper soil horizons is displaced as rainfall infiltrates the soils.

The loadings on the second factor are highest for Fe and Mn in all streams and capture between 8 % and 18 % of the variability within the original data sets. It is interpreted as the mobilisation of Fe and Mn at low pH within the soil and/or related to reductive solution of Fe and Mn oxyhydroxides in the soils under low redox conditions; the importance of such processes on stream chemistry has been widely recognised (Reid et al., 1981; Heal et al., 2002). Differences between individual streams mainly occur in the relative contribution of Fe and Mn to factor 2 as well as in the influence of other parameters on the loadings. In Winterhope Burn, for example, factor 2 shows an intermediate correlation with Mg and colour, while in Peaty Muckle Burn factor 2 includes intermediate Ca loadings (Table 3).

Q-mode analysis- Sample factor loading

Stream water samples from all streams show a similar spread of loading values on factor 1 and factor 2, the former being slightly larger.

Since data standardisation has been conducted prior to factor analysis, the determined R-and Q-mode factor loadings can be plotted in the same two-dimensional factor space. The resulting factor diagrams, demonstrated in Figure 7 for Shielhope Burn, not only illustrate the relationship of the samples to the original variables but also allow the sample loadings to be explained by reference to the position of the original variables in the same factor space. Samples with high negative loading on factor 1, for example, indicate a runoff composition dominated by high alkalinity, SiO_2 and base cation concentrations, while samples with high positive loadings reflect a high proportion of Al and colour in the stream runoff.

The temporal changes in sample factor loadings and their relation to flow are shown in Figure 8 and Figure 9. From the graphs it is clear that, as expected, factor 1 is closely related to flow, reinforcing the importance of flow path changes during storm events and the increasing influence of inputs from the upper, organic-rich soil horizons on stream flow composition. The importance of changes in flow path during events is also reflected in the factor plots as illustrated in Figure 10 for a single storm event. At the onset and during early stages of events when discharge is low, samples have high negative loadings on factor 1, hence the stream chemistry is close to baseflow composition. As the hydrograph rises, sample loadings on factor 1 steadily increase, reaching a maximum at peak flow. The associated maxima in colour and Al concentrations in the original data indicate that contributions from the upper organic-rich soil horizons are highest at peak flow. On the recession limb of the hydrograph, factor 1 loadings, and thus soil water inputs, gradually decline towards the initial negative values and baseflow composition.

Comparison between individual streams shows that loading patterns are similar for all streams (Figure 8 and Figure 9), but factor 1 loading values are generally highest at Shielhope Burn, indicating constantly higher soilwater contributions, associated with drainage from slow-draining peat soils. Samples from Peaty Muckle Burn and Winterhope Burn have lower loadings on factor 1, but these also increase considerably during storm events.

Factor 2 also shows some relation to flow (Figure 9), but appears to be less closely associated than factor 1. Factor 2 loadings in all streams are relatively small, except for a few samples collected during storm events. In the factor diagrams, these samples are easily identified as a small group of samples with high loadings on factor 2 (see encircled samples in Figure 7). During storm events, abrupt changes, noted as high factor 2 loadings, occur just before the hydrograph peaks and are followed by a rapid decline to pre-storm values (Figure 10). The sudden change in factor 2 loadings coincides with maximum Fe and Mn values in the original data and is interpreted as the displacement of deeper Fe and Mn-rich soilwater from the waterlogged gleyed soils in the riparian zone (Reid et al., 1981). This process is most pronounced in Shielhope Burn, which has the highest proportion of riparian gleyed soils. In Winterhope Burn and Peaty Muckle Burn, factor 2 loadings remain intermediate throughout the study period, suggesting small, but constant inputs of mobilised Fe and Mn through leaching from the more freely-draining soils. An increase in loading values is noted during storm events with maximum values foregoing the hydrograph peak; but peak values remain below those at Shielhope Burn. Following the storm events on 22-23 October and 24-25 October, a dramatic decline in factor 2 loadings is noted at both streams and thereafter factor 2 loadings remain low. Hence, it appears that during major storm events, the reservoir of mobilised Fe and Mn in the soils becomes depleted, and while replenishment is slow, contribution of this factor to stream chemistry remains low. The effects of antecedent conditions and storm magnitude on the stream chemistry are also illustrated in Figure 8 and Figure 9. The decrease in modulus of factor 2 loadings with successive storm events (Figure 9) suggests the gradual depletion of the reservoir of mobilised Fe and Mn in the riparian soils. The general shift of factor 1 loadings towards higher values (Figure 8) shows the increasing contribution of soilwater runoff in the wet catchments, illustrating the linkage between (soilwater) inputs from surface runoff /overland flow and storm magnitude.

The identification of two main factors also has implications for the End-Member Mixing Analysis. Statistical techniques similar to the one applied here have been used to aid ‘end-members’ identification (Christophersen and Hooper, 1992; Brown et al., 1999), assuming that the distinct properties of the different stream flow sources are reflected in the identified factors. The separation of two main factors, accounting for up to 90 % of the variability in the original data, would imply that at least three different ‘end-members’ are required to sufficiently explain stream chemistry variations (Christophersen and Hooper, 1992). These appear to be (1) a deeper soilwater/groundwater source, (2) an organic soilwater source from near-surface soil horizons with high colour loadings and rich in complexed Al, Fe and Mn and, (3) a deeper soilwater/groundwater source from the riparian zone rich in mobilised Fe and Mn. However, the latter only accounts for 8-15 % of the variability and cannot be distinguished using conservative hydrochemical tracers, such as alkalinity or Ca concentrations. Moreover, this component is clearly an Fe and Mn factor associated with displacement flow (translatory/piston flow) from the near-stream areas. It probably represents reduction processes occurring in the riparian soils rather than a separate runoff source since it acquires its signature by mixing subsurface stormflow from adjoining hillslopes with riparian groundwater. The importance of the riparian zone in effectively de-coupling sub-surface stormflow at the hillslope from the stream network has been demonstrated in a number of studies (Burns et al., 2001; Hangen et al., 2001; Smart et al., 2001). Therefore, the basic two-component approach is still considered adequate for the purpose of this modelling effort.

4.4 End-member mixing analysis

The hydrograph separations for the three streams are shown in Figure 11 for the period of intensive stream sampling. Uncertainty in the hydrograph split depends almost entirely upon the end-member selection, which in the case of the soilwater end-member was undertaken somewhat arbitrarily by means of literature data. To assess the effect of uncertainty in the soilwater end-member on the hydrograph separation, the proportion of groundwater contribution to flow is calculated for both an upper (alkalinity – 50 μEq l^{-1}) and a lower (alkalinity – 75 μEq l^{-1}) soilwater end-member (determined from literature Gran alkalinity values), which were chosen to represent the alkalinity range encountered in peaty podzols and peat soils (Ferrier et al., 1990; Soulsby and Dunn, 2003; Soulsby et al., 2003). Figure 11 illustrates that errors in groundwater proportion are small (1-5 %) in all streams and approximately constant with time, with greatest divergence occurring at high flows.

In each catchment inputs from the upper, organic-rich soil horizons have a major influence on stream hydrochemistry during storm events (Figure 11). Depending on storm magnitude, soilwater contributions are often large enough to dominate stream chemistry and override the groundwater signal, although a significant proportion of deep water is also reaching the stream during these runoff periods. In individual streams, groundwater still contributes between 26 % and 43 % of flow at maximum flow.

Groundwater inputs dominate the stream chemistry during periods of low flow as well as during hydrograph rise and, except for the smaller catchment of Peaty Muckle Burn (Figure 11c), peak about 1-2 hours before the peak of the soilwater end-member, which typically occurs at maximum flow. This early groundwater peak is probably associated with the displacement of deep soilwater and groundwater as subsurface flow from the steeper hillslopes enters the riparian zone (Giusti and Neal, 1993). The process is more pronounced in Shielhope Burn (Figure 11b), probably due to the high proportion of waterlogged gley soils in the riparian area, which also promotes the reduction of Fe and Mn and the subsequent flushing of Fe and Mn into the stream along with displaced riparian groundwater (Reid et al., 1981). It is also seen in Winterhope Burn (Figure 11a) but in Peaty Muckle Burn, flushing of riparian groundwater is less distinct probably due to the smaller catchment area and the less developed riparian zone.

Differences in the response between individual catchments during events are also apparent from the graphs. In Shielhope Burn, the sharp rise in soilwater contribution during events and the slow decline (long recession limb) of the hydrograph are consistent with the generally flashier soilwater response followed by the slow movement of throughflow fed by the large surface-storage reservoir of the organic-rich soils which dominate the catchment area. The high proportion of poorly-draining peat soils in the catchment is also responsible for the comparatively high contribution of the organic-rich soilwater component (29 %-47 %) at low flows. During the sampled events, soilwater contributes up to 74 % of the flow at Shielhope Burn, but higher soilwater contributions are likely to occur during larger events (e.g., 25 October 2000), not sampled at this stream. A rapid increase in soilwater influence during stormflow is also seen at Winterhope Burn and Peaty Muckle Burn, but during small events, soilwater contribution at these streams does not exceed that of groundwater. The constant increase in the low flow soilwater contribution with successive storm events, seen at all streams, confirms that antecedent conditions in the catchment influence the stream chemical signal.

In order to estimate groundwater proportions over longer periods from the time series of flow data, the strong relationship between flow and percent groundwater (here gw lower was employed) for the Winterhope Burn (Figure 12) was used to reconstruct the entire streamwater time series (August 2000 to December 2001) for the Winterhope Burn (Foster, 2000; Jarvie et al., 2001). Applying the fitted equations to the time-series flow data resulted in a hydrograph separation displayed in Figure 13. The graph clearly reflects the annual variations in the contribution of the two flow components, with high groundwater proportions dominating summer flow (May-August), diluted by soilwater inputs during the wetter autumn and winter period (September-January) and during spring storm events. The graph also highlights periods during which high amounts of soilwater are transported by the streams, and such information is very valuable for catchment management purposes, as soilwater from organic rich peat are associated with high loadings in colour and complexed metals. With regard to the Megget Reservoir, the graphs imply that the bulk of Fe and Mn is delivered to the reservoir during autumn and winter storm events rather than during the drier summer months. To test the ability of the EMMA model to reconstruct stream water composition from flow data, the strong linear correlation (R^2=0.85) between measured Ca concentrations (Ca_{stream}) in the streams and percent groundwater ($\%gw$) given by the equation:

$$Ca_{stream}=3.7865 * \%gw - 0.008 \qquad (Eq\ 4)$$

was used to model stream Ca concentrations. An equation, relating Ca and flow, was fitted to the data and using the previously derived EMMA model, Ca concentrations were then predicted from the flow data for all three streams. The results were compared with measured Ca concentrations by means of regression analysis (Smith, 1998) and the linear regression relations between predicted and measured Ca concentrations are given in Table 4. The coefficients of determination (R^2) of 0.87, 0.88 and 0.86 for Shielhope Burn, Winterhope Burn and Peaty Muckle Burn provide evidence that the separations predicted by EMMA appear to be realistic. However, in all three cases, the *slope* of the regression equation was found to be statistically different from 1 and its *intercept* statistically different from 0. This implies that, while the general trends are well captured by the model, further improvement is required for predicting absolute values.

5 Discussion and Conclusions

The data collected during the intensive sampling programme and analyses undertaken since then clearly highlight the utility of short-term sampling during storm events for catchment studies, the importance of which is widely recognised in the hydrological community (Peters, 1994; Longabucco and Rafferty, 1998; Foster, 2000; Jarvie et al., 2001). While substantiating the general trends observed during routine sampling, event-sampling details the rapid changes in stream chemistry during events and thereby exposes the wide range of stream chemical loadings that occur in individual streams.

Factor analysis was successfully applied to the data and the results clearly demonstrate that flow related changes in soilwater inputs (associated with changes in flow pathways) exert a major control on stream chemistry during storm events. One could rightfully argue that flow related changes in stream chemistry emerge as the principal factor, simply because the variables in the input data set are highly correlated to flow. This demonstrates the close link between flow pattern and stream chemistry and emphasizes the important influence of changing hydrological pathways during storm events on stream composition in upland regions (see reviews in Church, 1997 and Soulsby, 1997).

Two Fe and Mn sources are identified within the studied catchments: (1) an organic soilwater source, associated with the accumulation of organically complexed Fe and

Mn in organic-rich soil horizons and (2) a deep soilwater/groundwater source related to metal mobilisation at low pH and/or reductive solution of Fe and Mn oxides and hydroxides under low redox conditions in deeper soils of the riparian zone. The contribution of the two sources varies between individual catchments and also depends on antecedent conditions and storm magnitude. The organic soilwater source is typically the dominant Fe and Mn source during storm events, where runoff from organic soil horizons increases, and maximum contribution from that source occurs at peak discharge. It also shows a positive relationship to storm magnitude and this is consistent with the finding that the contribution of pre-event water to runoff increases with increasing rainfall intensity and amount (Giusti and Neal, 1993; Burns et al., 2001). In the peat-dominated Shielhope catchment, the high proportion of organic rich soils not only provides a suitable substrate for the formation of a large store of readily soluble Fe and Mn, but the waterlogged and/or poorly-draining peaty soils also contribute water to the baseflow very slowly (Rees et al., 1989; Giusti and Neal, 1993), thus providing constant Fe and Mn inputs into the stream, even during low flow periods.

EMMA is clearly a simple, but powerful tool for assessing the contribution of the different runoff sources to the stream hydrograph. The hydrograph separation presented here gives a first approximation of the changing soilwater and groundwater influence at the different catchments during the sampling period. The results show that soilwater has a major influence on the stream hydrochemistry during events and is large enough to dominate stream chemistry and override the groundwater signal, although a significant portion of deep water is also reaching the stream during these runoff periods. Such buffering of stream water chemistry by groundwater inputs at high flows has also been reported in other Scottish upland catchments (Giusti and Neal, 1993; Soulsby et al., 1998) and is mainly attributed to inputs from riparian areas and from valley bottom glacial deposits. While these areas are mostly fed by recharge from the freely-draining alpine soils in the upper parts of the catchment, bedrock fractures may also act as flow pathways during storm events (Hill and Neal, 1997, Neal et al., 1997a), so that inputs from a dynamic groundwater component are also possible.

The results further reflect the effects of soil type distribution on stream chemistry, in particular with respect to Fe and Mn loading and stormflow response. High loadings in colour and organically complexed metals are generally associated with high proportions of organic rich soils in the catchment area (Aitkenhead et al., 1999; Dawson et al., 2001, Graham et al., 2002) which not only provide peak runoff, but can also give rise to a permanent, though small, organic rich flow component (Rees et al., 1989; Giusti and Neal, 1993; Stunell and Younger, 1995; Holden and Burt, 2000). Both, magnitude and exact timing of groundwater and soilwater peaks appear to be strongly dependent on antecedent conditions and storm intensity and such relationships between catchment wetness, storm magnitude and quantity of runoff from the different in-catchment stores are well-documented for a wide range of catchment settings (Giusti and Neal, 1993; Robson et al., 1993; Hoeg et al., 2000; Burns et al., 2001).

The timing of maximum annual Fe and Mn concentrations in runoff has important implications for water supply management in upland catchments. In this study, the critical periods for high Fe and Mn concentrations (often in excess of 200 μg l^{-1} and

50 µg l^{-1}- the maximum admissible concentrations in drinking water) in stream runoff are identified as autumn and winter storm events, during which the bulk of Fe and Mn is delivered to the Megget Reservoir. These results are consistent with Reid et al. (1981) and Giusti and Neal (1993), but should not be generalised, as in some upland catchments high levels in Mn and Fe are reported during summer baseflow (Stunell and Younger, 1995; Heal et al., 2002). In the Megget catchment, loadings may be markedly higher during the first autumn storms, particularly after a dry summer period, during which Fe and Mn accumulate in the shallow soils (Graham et al., 2002, Neal et al., 1997a) as a results of high soil microbial activity and organic matter breakdown and in the deeper soils due to mobilisation and release of Fe and Mn from bedrock sources under low pH and/or redox conditions. These high loadings will probably decrease with successive storm events as the (deeper) soil reservoirs become gradually depleted. However, a better knowledge and understanding of the nature of the different sources, in particular the deeper source, is necessary to better predict when and where undesirable Fe and Mn concentrations will occur.

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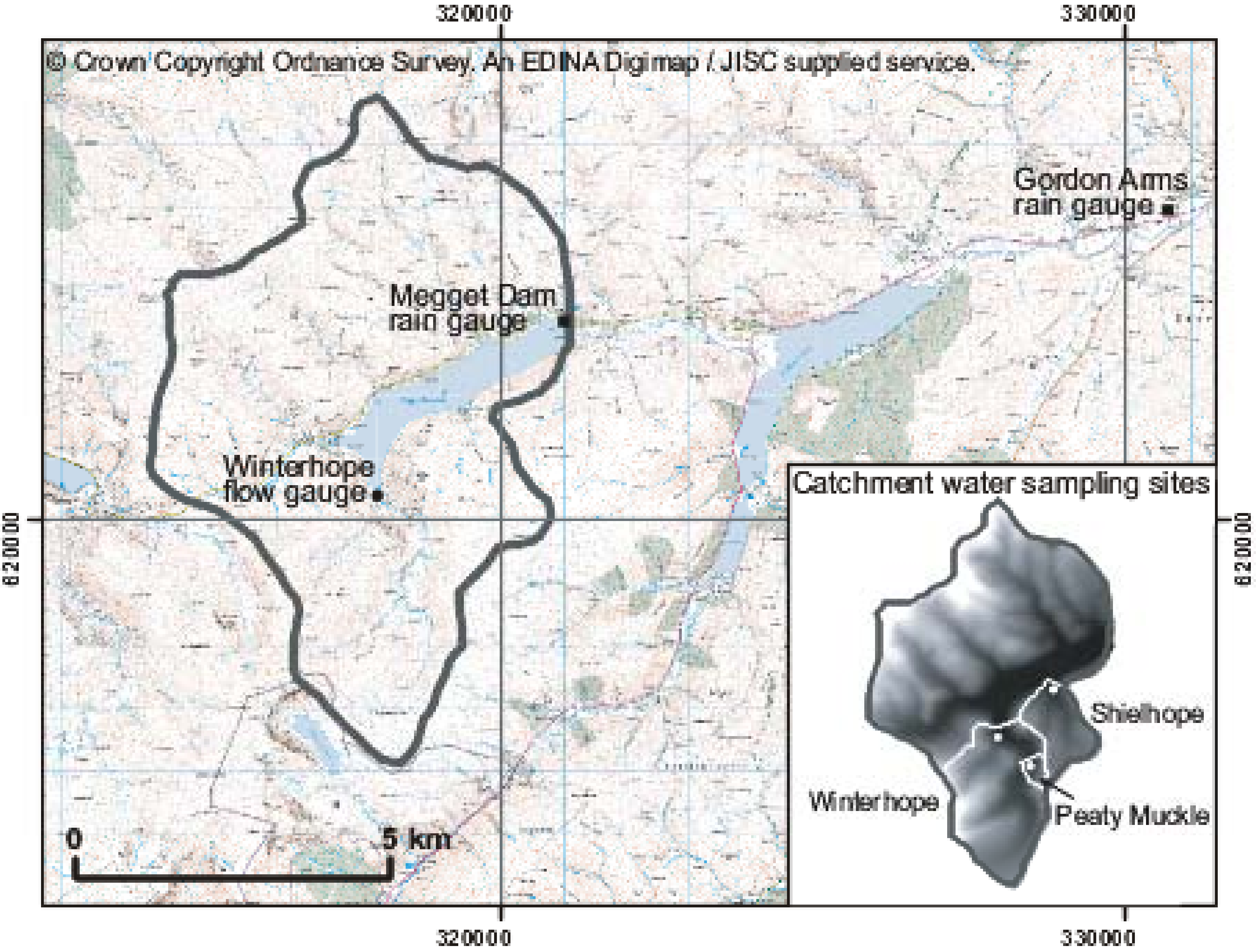


320000
330000
© Crown Copyright Ordnance Survey. An EDINA Digimap / JISC supplied service.
Gordon Arms rain gauge
Megget Dam rain gauge
Winterhope flow gauge
Catchment water sampling sites
Shielhope
Winterhope
Peaty Muckle
0
5 km
620000

Figure 1

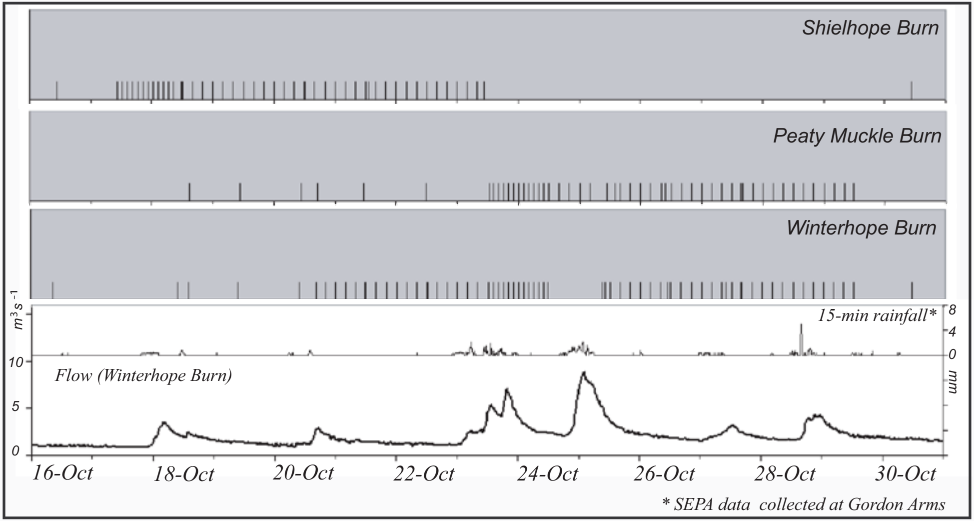
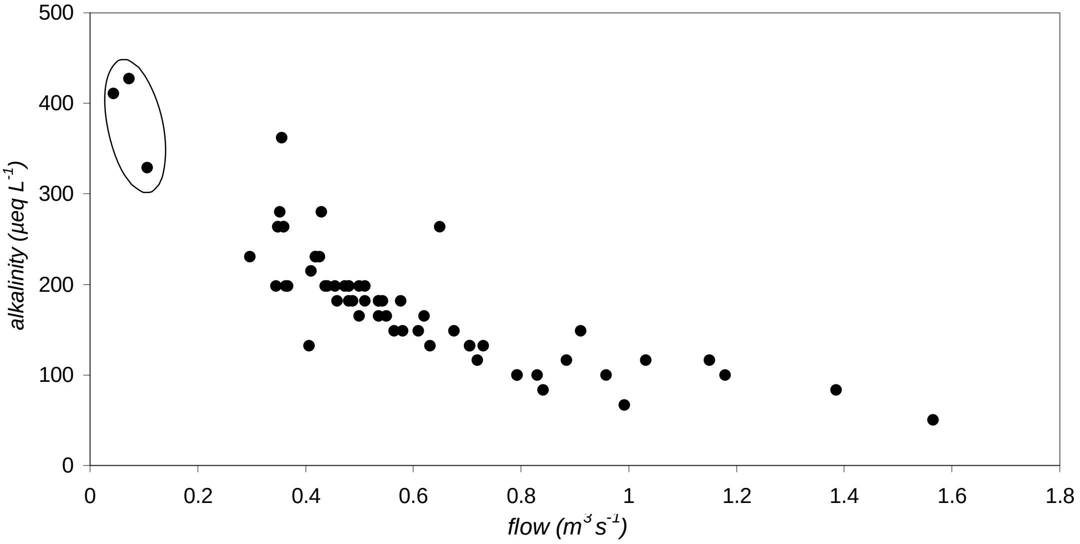
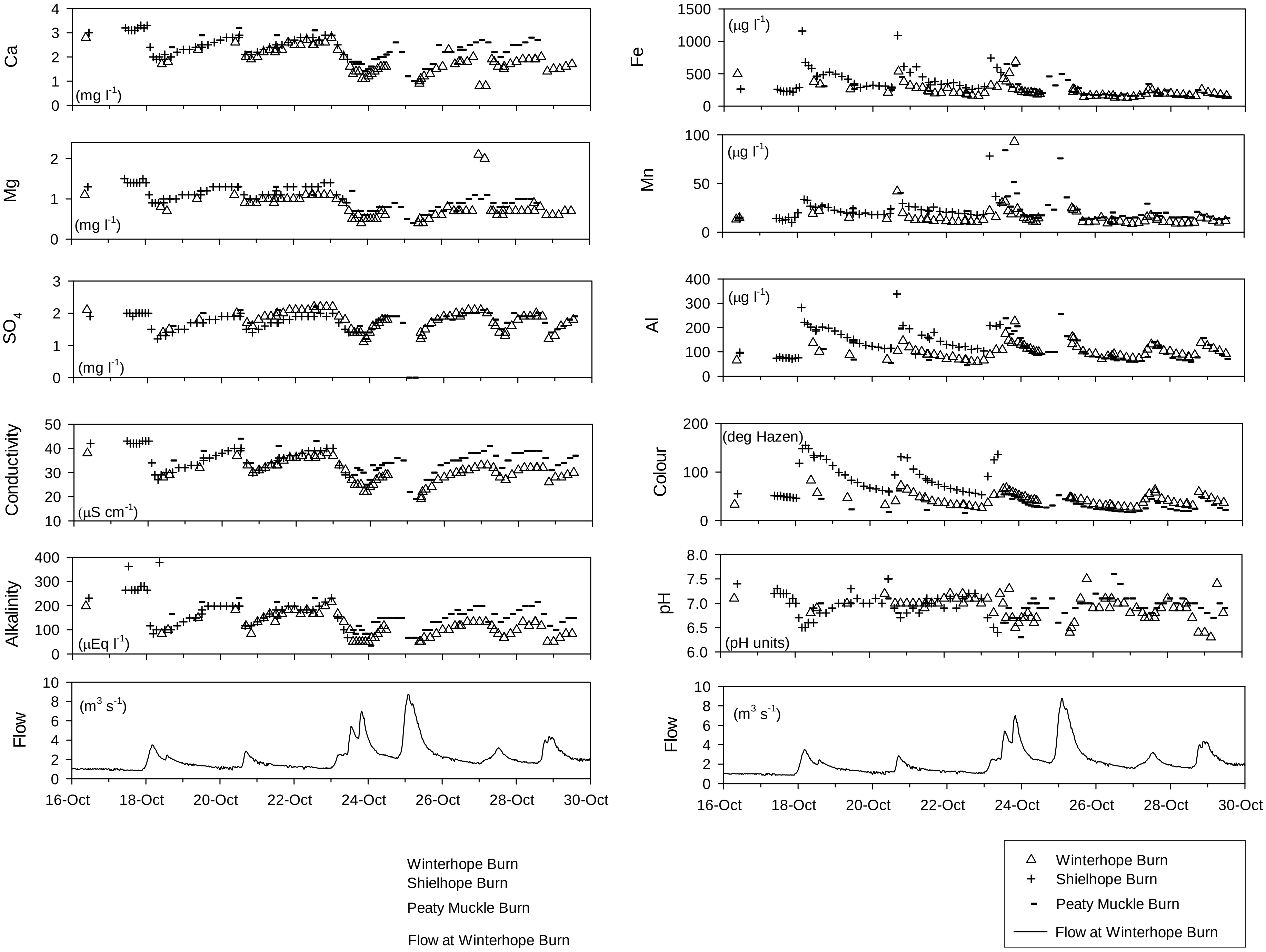

Shielhope Burn
Peaty Muckle Burn
Winterhope Burn
$m^3 s^{-1}$
15-min rainfall*
8
4
0
mm
10
5
0
Flow (Winterhope Burn)
16-Oct
18-Oct
20-Oct
22-Oct
24-Oct
26-Oct
28-Oct
30-Oct
* SEPA data collected at Gordon Arms

Figure 2


500
400
300
200
100
0
alkalinity (μeq L⁻¹)
0
0.2
0.4
0.6
0.8
1
1.2
1.4
1.6
1.8
flow (m³ s⁻¹)


Ca
(mg l-1)
Mg
(mg l-1)
SO4
(mg l-1)
Conductivity
(µS cm-1)
Alkalinity
(µEq l-1)
Flow
(m3 s-1)
Fe
(µg l-1)
Mn
(µg l-1)
Al
(µg l-1)
Colour
(deg Hazen)
pH
(pH units)
Flow
(m3 s-1)
16-Oct
18-Oct
20-Oct
22-Oct
24-Oct
26-Oct
28-Oct
30-Oct
Winterhope Burn
Shielhope Burn
Peaty Muckle Burn
Flow at Winterhope Burn
△ Winterhope Burn
+ Shielhope Burn
- Peaty Muckle Burn
Flow at Winterhope Burn

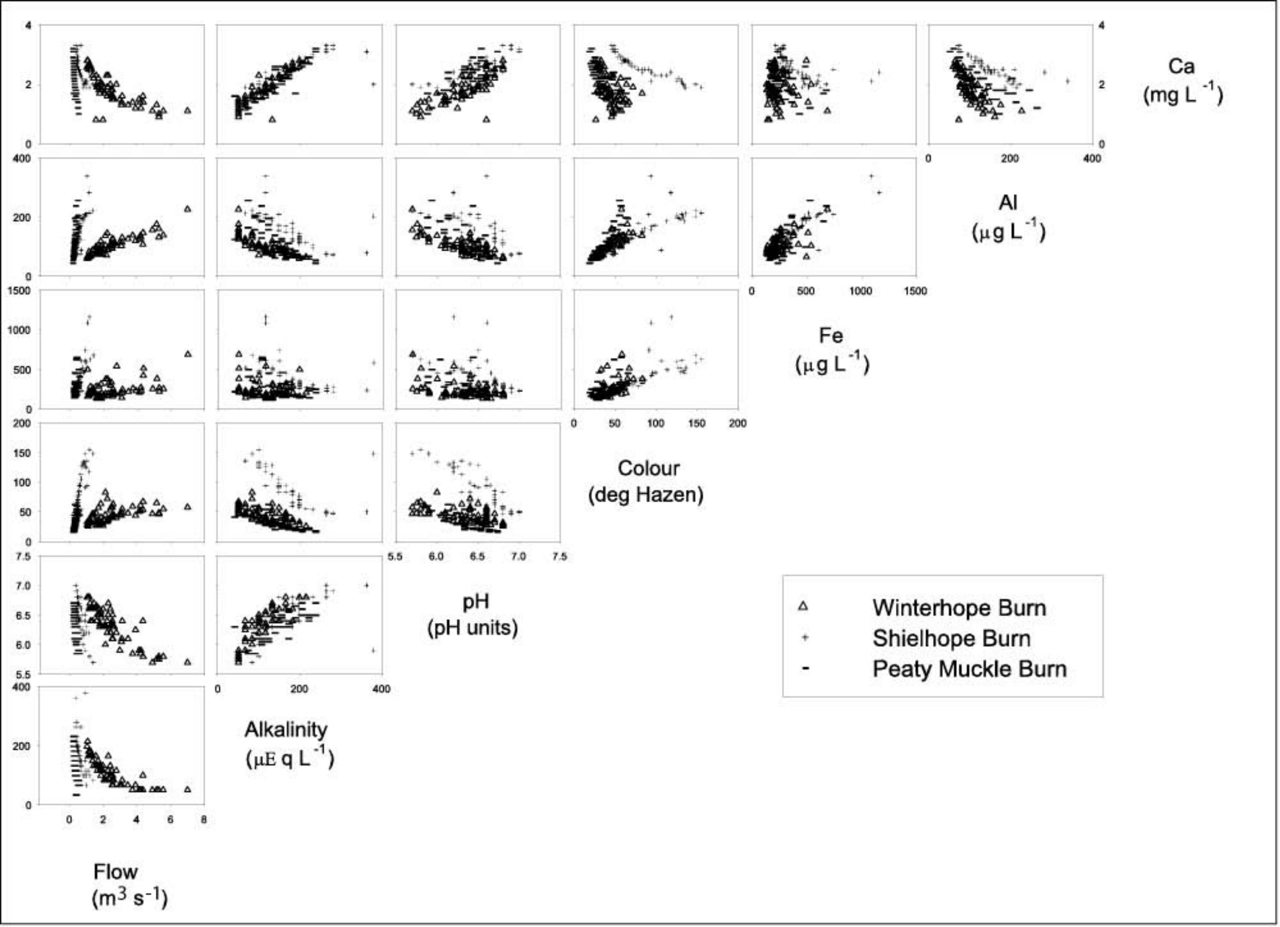
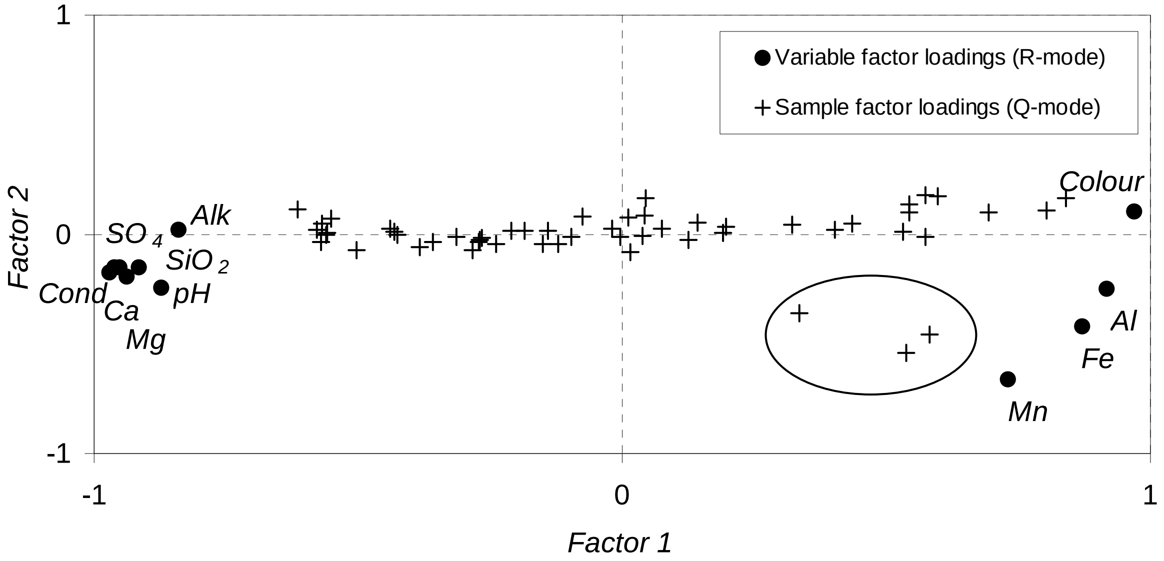
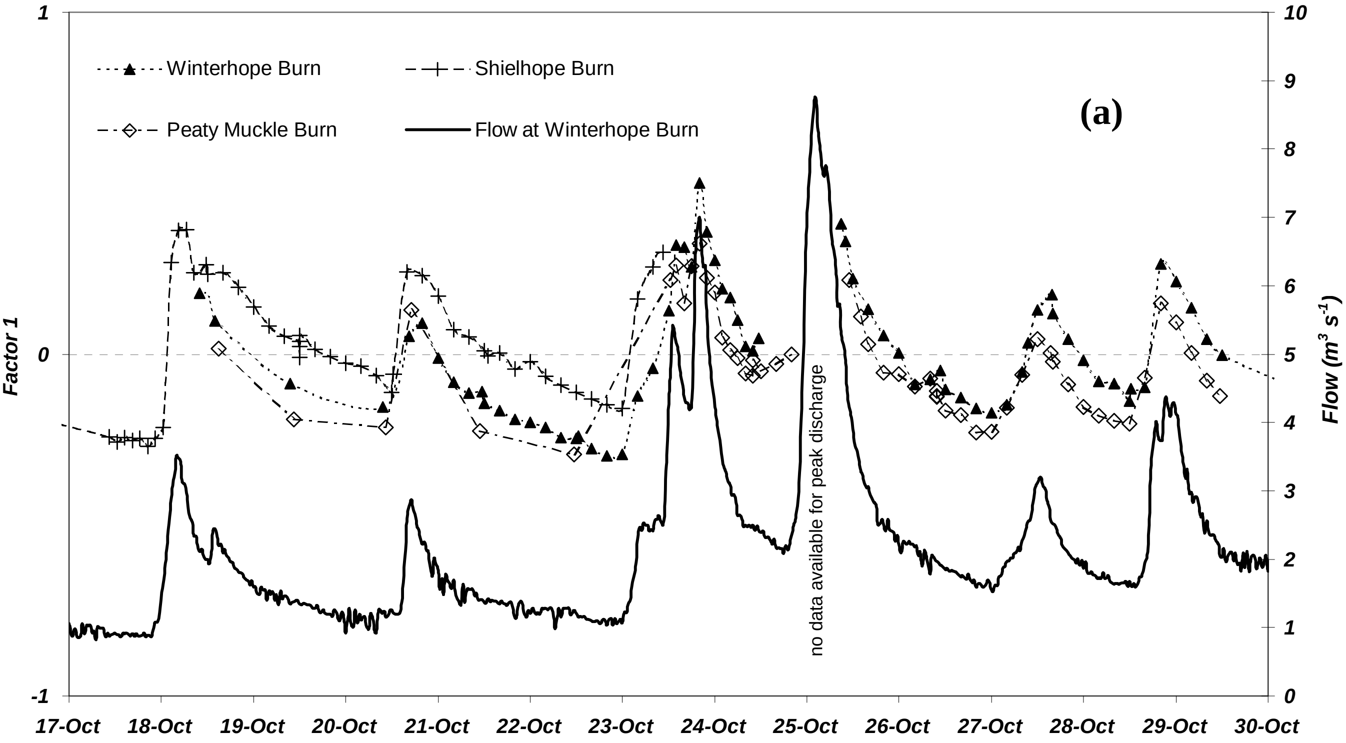

Ca
(mg L -1)
Al
(μg L -1)
Fe
(μg L -1)
Colour
(deg Hazen)
pH
(pH units)
Alkalinity
(μEq L -1)
Flow
(m3 s-1)
0
2
4
0
200
400
0
500
1000
1500
0
50
100
150
200
5.5
6.0
6.5
7.0
7.5
0
2
4
6
8
Winterhope Burn
Shielhope Burn
Peaty Muckle Burn

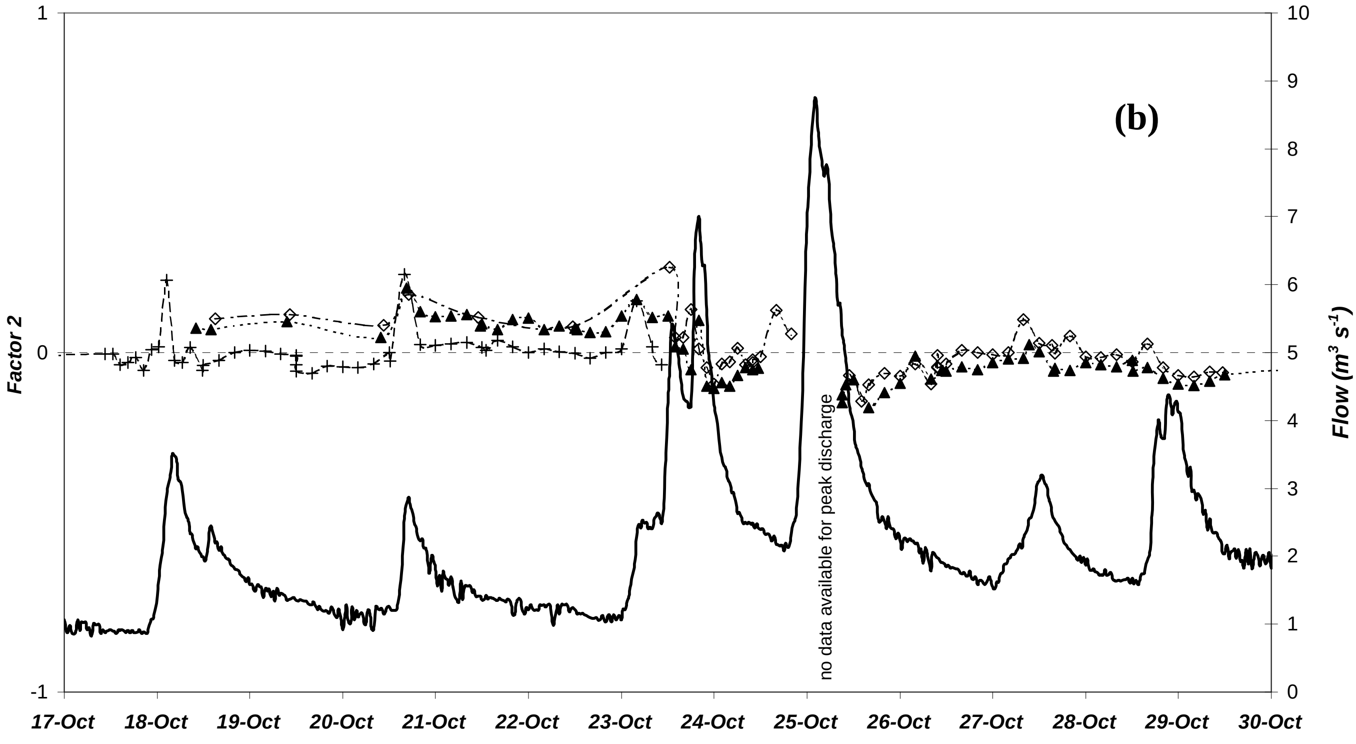
Figure 6



● Variable factor loadings (R-mode)
+ Sample factor loadings (Q-mode)
1
0
-1
Factor 2
-1
0
1
Factor 1
Alk
SO 4
SiO 2
Cond
Ca
pH
Mg
Colour
Al
Fe
Mn

Figure 7


Winterhope Burn
Shielhope Burn
Peaty Muckle Burn
Flow at Winterhope Burn
(a)
Factor 1
1
0
-1
Flow ($m^3 s^{-1}$)
10
9
8
7
6
5
4
3
2
1
0
no data available for peak discharge
17-Oct
18-Oct
19-Oct
20-Oct
21-Oct
22-Oct
23-Oct
24-Oct
25-Oct
26-Oct
27-Oct
28-Oct
29-Oct
30-Oct


(b)
Factor 2
1
0
-1
Flow ($m^3 s^{-1}$)
10
9
8
7
6
5
4
3
2
1
0
no data available for peak discharge
17-Oct
18-Oct
19-Oct
20-Oct
21-Oct
22-Oct
23-Oct
24-Oct
25-Oct
26-Oct
27-Oct
28-Oct
29-Oct
30-Oct

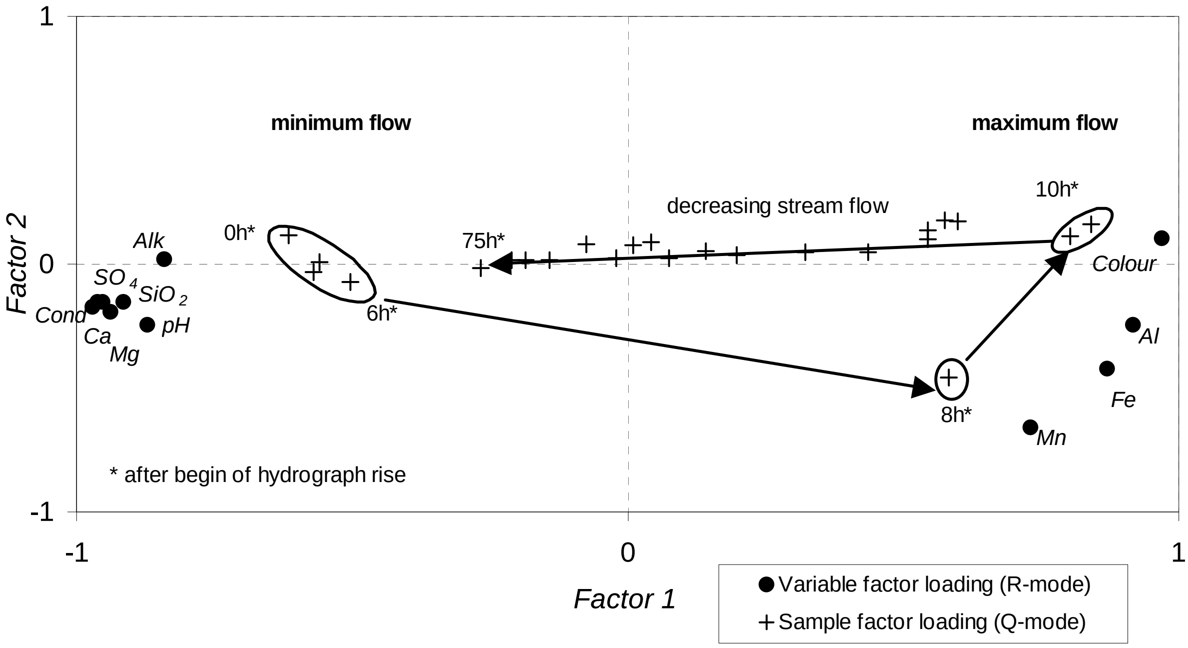

1
0
-1
Factor 2
-1
0
1
Factor 1
minimum flow
maximum flow
decreasing stream flow
10h*
0h*
75h*
6h*
8h*
Alk
SO 4
SiO 2
Cond
Ca
Mg
pH
Colour
Al
Fe
Mn
* after begin of hydrograph rise
● Variable factor loading (R-mode)
+ Sample factor loading (Q-mode)

Figure 10

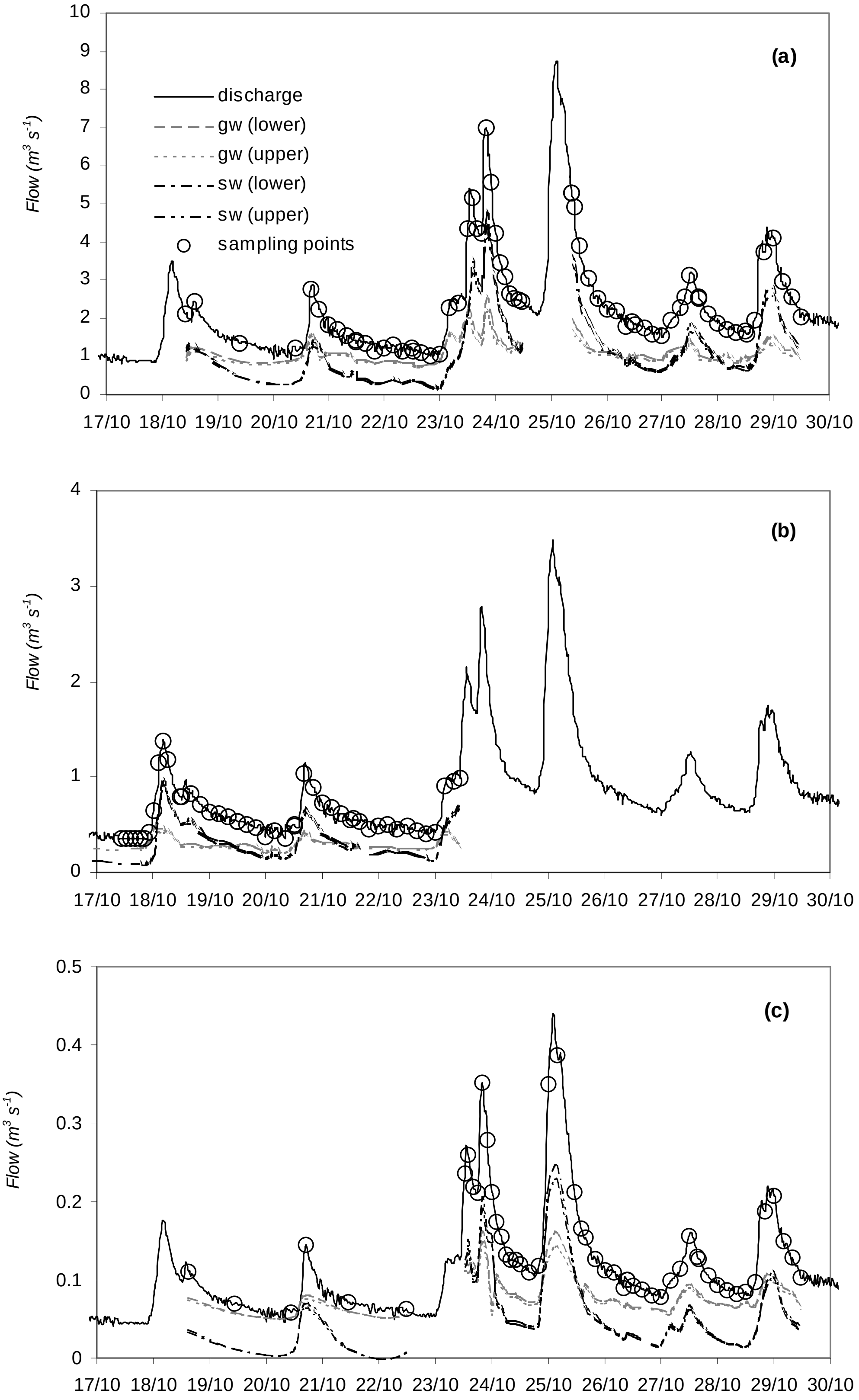

(a)
Flow ($m^3 s^{-1}$)
discharge
gw (lower)
gw (upper)
sw (lower)
sw (upper)
sampling points
0
1
2
3
4
5
6
7
8
9
10
17/10 18/10 19/10 20/10 21/10 22/10 23/10 24/10 25/10 26/10 27/10 28/10 29/10 30/10
(b)
Flow ($m^3 s^{-1}$)
0
1
2
3
4
17/10 18/10 19/10 20/10 21/10 22/10 23/10 24/10 25/10 26/10 27/10 28/10 29/10 30/10
(c)
Flow ($m^3 s^{-1}$)
0
0.1
0.2
0.3
0.4
0.5
17/10 18/10 19/10 20/10 21/10 22/10 23/10 24/10 25/10 26/10 27/10 28/10 29/10 30/10

Figure 11

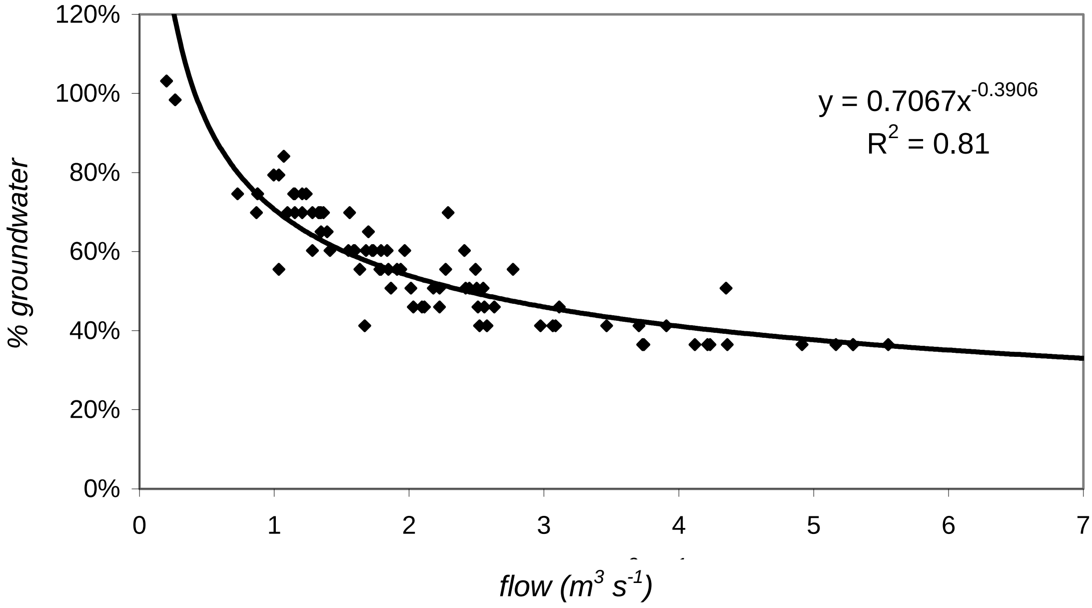

120%
100%
80%
60%
40%
20%
0%
% groundwater
0
1
2
3
4
5
6
7
flow (m3 s-1)
y = 0.7067x-0.3906
R2 = 0.81

Figure 12

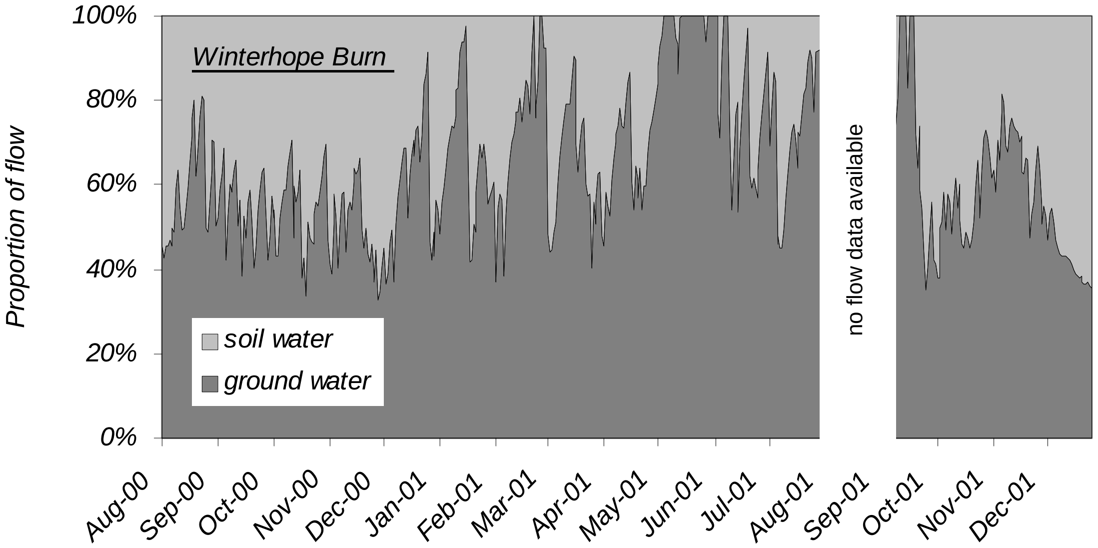

Winterhope Burn
Proportion of flow
100%
80%
60%
40%
20%
0%
soil water
ground water
no flow data available
Aug-00
Sep-00
Oct-00
Nov-00
Dec-00
Jan-01
Feb-01
Mar-01
Apr-01
May-01
Jun-01
Jul-01
Aug-01
Sep-01
Oct-01
Nov-01
Dec-01

Figure 13

Figure 14

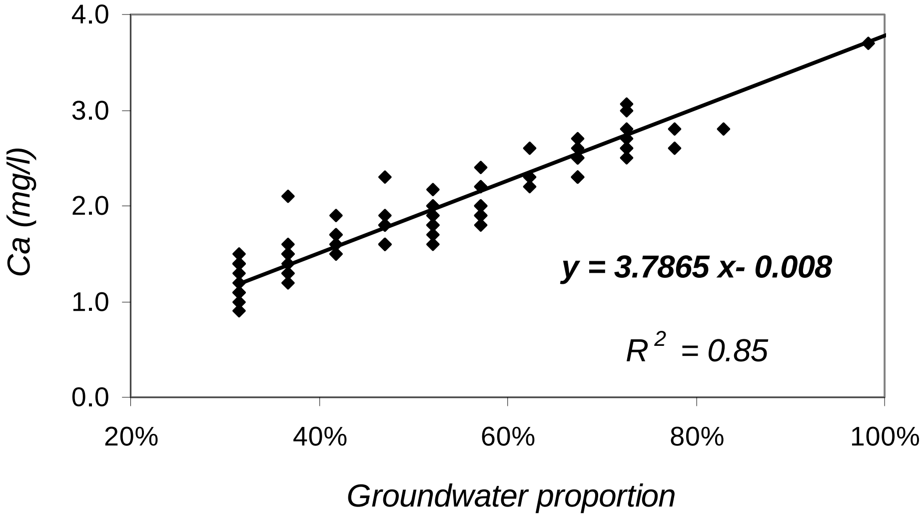

4.0
3.0
2.0
1.0
0.0
Ca (mg/l)
y = 3.7865 x- 0.008
R 2 = 0.85
20%
40%
60%
80%
100%
Groundwater proportion

Figure 15

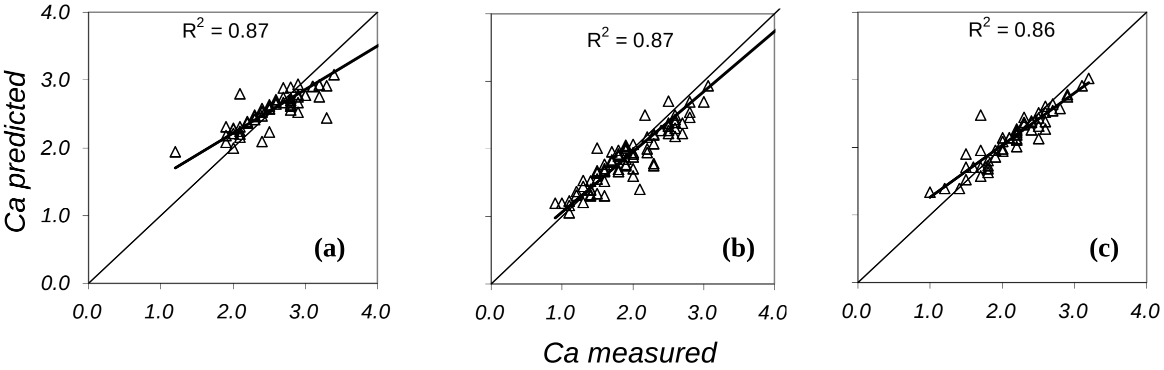


Table 1

				*Slope angle (°)**				*Soil type proportions (%)*			
	*Catchment Area (km^2)**	*Length/width ratio**	*Maximum elevation* (m above sea level)*	*Maximum*	*Mean*	*Standard deviation*	*Average daily flow (cumecs)***	*Blanket peat*	*Peaty podzols*	*Peaty gleys / some peaty podzols*	*Others*
Winterhope Burn	10.3	2.04	801	43.8	15.6	8.7	1.8	38	31	2	29
Peaty Muckle	0.5		588				0.1	50	50	0	0
Shielhope Burn	4.1	2.03	588	27.7	9.5	5.08	0.7	52	0	46	2

* *derived from Digimap Digital Elevation Model (DEM)*
** *estimated from flow measurements at Winterhope Burn between 7 Aug 2000 and 9 April 2002*

Table 2

	*Groundwater end-member**	*Soilwater end-member ***	
Winterhope Burn	269	-75	-50
Peaty Muckle Burn	269	-75	-50
Shielhope Burn	389	-75	-50

(calculated from alkalinities at three lowest flows, ** estimated from literature values in Ferrier et al. (1990), Soulsby et al. (2003); Soulsby and Dunn (2003); Soulsby (unpublished data))*

Table 3

	Winterhope Burn			Shielhope Burn			Peaty Muckle Burn		
Elements	Factor 1	Factor 2		Factor 1	Factor 2		Factor 1	Factor 2	
Colour	0.765	–0.406		0.969	0.104		0.912	–0.192	
Conductivity	–0.909	–0.255		–0.971	–0.174		–0.839	–0.157	
PH	–0.909	–0.191		–0.872	–0.246		–0.772	0.009	
Alkalinity	–0.945	–0.238		–0.841	0.019		–0.854	–0.140	
Mn	0.687	–0.571		0.731	–0.660		0.487	–0.848	
Fe	0.448	–0.860		0.871	–0.422		0.550	–0.771	
Al	0.947	–0.149		0.917	–0.247		0.941	–0.214	
Ca	–0.807	–0.239		–0.938	–0.192		–0.721	–0.590	
Mg	–0.733	–0.419		–0.962	–0.152		–0.899	–0.330	
SiO2	–0.966	–0.188		–0.914	–0.151		–0.926	–0.320	
SO4	–0.953	0.086		–0.952	–0.152		–0.933	–0.052	
Eigenvalues	7.728	1.687	Total:	9.032	0.882	Total:	7.343	2.001	Total:
Variance explained (%)	70	15	85	82	8	90	67	18	85