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A hydrochemical modelling framework for combined assessment of spatial and temporal variability in stream chemistry: application to Plynlimon, Wales

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Abstract

Recent concern about the risk to biota from acidification in upland areas, due to air pollution and land-use change (such as the planting of coniferous forests), has generated a need to model catchment hydro-chemistry to assess environmental risk and define protection strategies. Previous approaches have tended to concentrate on quantifying either spatial variability at a regional scale or temporal variability at a given location. However, to protect biota from 'acid episodes', an assessment of both temporal and spatial variability of stream chemistry is required at a catchment scale. In addition, quantification of temporal variability needs to represent both episodic event response and long term variability caused by deposition and/or land-use change. Both spatial and temporal variability in streamwater chemistry are considered in a new modelling methodology based on application to the Plynlimon catchments, central Wales. A two-component End-Member Mixing Analysis (EMMA) is used whereby low and high flow chemistry are taken to represent 'groundwater' and 'soil water' end-members. The conventional EMMA method is extended to incorporate spatial variability in the two end-members across the catchments by quantifying the Acid Neutralisation Capacity (ANC) of each in terms of a statistical distribution. These are then input as stochastic variables to a two-component mixing model, thereby accounting for variability of ANC both spatially and temporally. The model is coupled to a long-term acidification model (MAGIC) to predict the evolution of the end members and, hence, the response to future scenarios. The results can be plotted as a function of time and space, which enables better assessment of the likely effects of pollution deposition or land-use changes in the future on the stream chemistry than current methods which use catchment average values. The model is also a useful basis for further research into linkage between hydrochemistry and intra-catchment biological diversity.

Keywords: hydrochemistry, End-Member Mixing Analysis (EMMA), uplands, acidification

Introduction

Hydrochemical modelling of upland catchments is an important tool for assessing the impacts of pollutant deposition and land-use change on stream chemistry. Upland areas typically have thin acidic soils and a low buffering capacity, which makes them susceptible to acidification. The streams also have a flashy hydrological response, which is accompanied by rapid changes in stream chemistry, such as increased acidity and aluminium concentrations during high flows. These 'acid episodes' may result in the death of fish

and other biological organisms (Ormerod and Jenkins, 1994). In addition, afforestation in such areas has been suspected of exacerbating the problem (Jenkins *et al.*, 1990; Harriman *et al.*, 1994).

End-Member Mixing Analysis (EMMA, Christophersen *et al.*, 1990) is commonly used to predict episodic variability in stream chemistry and, when coupled with the long-term hydrochemical simulation model MAGIC (Cosby *et al.*, 1985a,b), enables prediction of future temporal changes (Neal *et al.*, 1992; Wade, 1999). Other methods of stream chemistry prediction consider spatial variability (Billett and Cresser, 1992; Hornung *et al.*, 1990). Indeed, at the subcatchment and the small catchment (<50 ha) scale, tackling the high heterogeneity encountered is a major task (Hill and Neal,

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1997; Neal *et al.*, 1997a, 1998). Thus, the problem of how to combine these techniques and incorporate both temporal variability and spatial heterogeneity into an integrated modelling strategy for catchment management purposes is of growing importance (Neal, 1997). The concept of 'critical loads', applied for policy decision making purposes (e.g. CLAG, 1994) has been adopted throughout Europe and accounts for large scale spatial variability. Although MAGIC has been used to incorporate critical load time dependence at a site (Jenkins *et al.*, 1997a) and has been extended to consider the regional picture (Sefton and Jenkins, 1998), spatial variability at the catchment level has not been addressed.

In this paper, the headwater catchments of the River Severn at Plynlimon, Wales, are used as a case study to consider both temporal and spatial variability of catchment hydrochemistry. A new modelling framework is presented to quantify catchment hydrochemical variability in time and space so that improved predictions can be made in assessment of pollution abatement strategies.

Site information and stream chemistry data

The upper Severn catchments have been the focus of extensive hydrological research since 1968 (Kirby *et al.*,

1991). Located in central Wales, 24km inland from the Irish Sea, they cover an area of 870 ha and range in altitude from 320 to 740 m. Streams are of first to third order (Fig. 1). The soils are typical of acid upland soils, consisting of peats, stagnopodzols, acid brown earths and stagnogleys, with local drift deposits of colluvium and valley bottom alluvium. The geology is base-poor, with undivided mudstones, shales and grits of upper Ordovician and Silurian age. Land-use consists of plantation forestry of Sitka Spruce (*Picea sitchensis*) and Norway Spruce (*Picea abies*) in various phases of felling and replanting, with semi-natural acidic moorland covering the upper regions. The hydrological response of the streams is 'flashy', responding rapidly to rainfall events, and the area is also vulnerable to the effects of pollutant deposition which has acidified soils and waters.

Extensive stream chemistry data are available for these catchments. Weekly stream chemistry has been monitored at 10 sites on first to third order streams for up to 15 years by the Centre for Ecology and Hydrology (CEH) (Reynolds *et al.*, 1989; Neal *et al.*, 1997b) and continuous flow and pH data are available for the larger streams (Robson, 1993; Hodgson and Evans, 1997). In addition, daily and three-hourly episodic storm sampling has been undertaken at 6 sites and one-off low flow samples during the summer of 1996 at 40 sites by Imperial College and CEH working in partnership (Locks, 1996; Foster *et al.*, 1997, 2001).
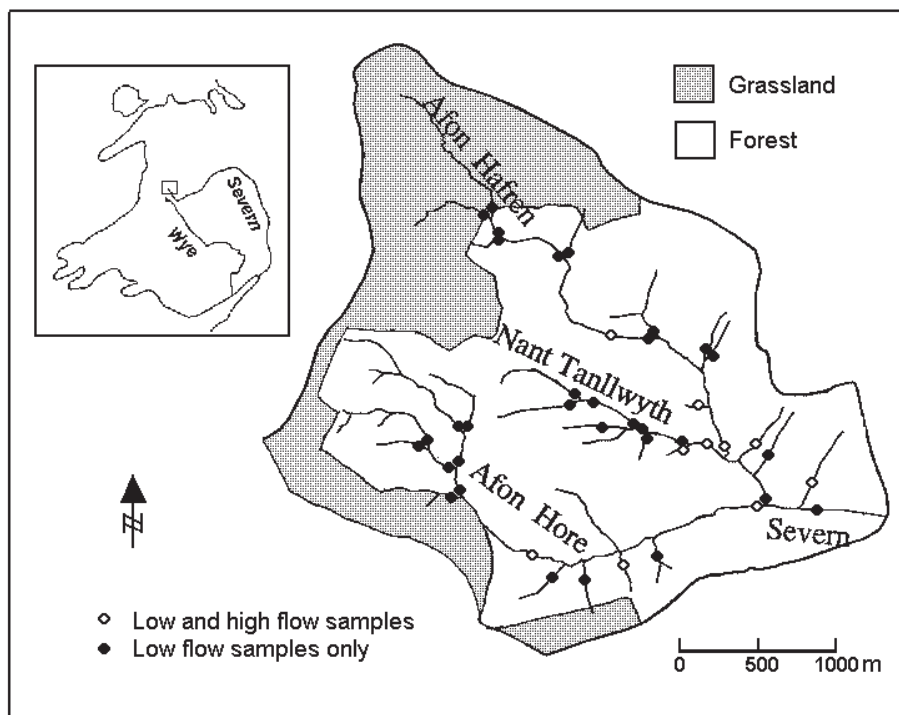

Fig. 1. *The Plynlimon catchments: Location, land-use and low and high flow sampling sites.*

Modelling temporal variability in streamwater chemistry using EMMA

The change in relative contributions of water from different sources and along differing flow pathways during a storm event is the primary factor which influences rapid stream hydrochemical variations at these times (Wheater *et al.*, 1990, 1993; Muscutt *et al.*, 1993). Because 'piston flow' takes place at Plynlimon, much of the rainwater remains in the catchment and is rapidly affected by processes such as cation exchange, only later being transferred to the stream by successive episodes (Robson, 1993). The rainfall signal is seen only rarely in the stream, during very large rainfall events, and stream chemical response is therefore generally related to flow (Neal *et al.*, 1997a). It is also scale-, soil- and groundwater dependent (Chapman *et al.*, 1993, 1997; Neal *et al.*, 1997a, 1998). On examination of the temporal variability of chemistry and effects of scale within the Severn catchments, Foster *et al.* (1997) found that first order tributaries, and also the main streams themselves during high flows, may be considered as representing an 'integrated' measure of soil water chemistry. At high flows, this acidic soil-water is the main component of flow and, at other times, there is a more alkaline water source, probably a deeper subsurface component of stream-flow (Hill and Neal, 1997; Neal *et al.*, 1997a).

Therefore, a conceptual model may be proposed, whereby streamwater is thought of as consisting of two or more 'end-members' with different chemistries, the proportions of which change with discharge (Wheater *et al.*, 1990; Christophersen *et al.*, 1990; Robson and Neal, 1990; Neal *et al.*, 1992). During periods of low flow, a stream is fed mainly by water from the lower soil horizons and deeper groundwater, which typically has a high Acid Neutralisation Capacity (ANC) and low acidity, due to the weathering of base cations in the lower soil horizons and bedrock (Neal *et al.*, 1990). However, during a rainfall event, most flow is derived from the upper, more acidic and aluminium-bearing soil horizons, causing the stream chemistry to alter dramatically.

This conceptual model underlies two-component End-Member Mixing Analysis (EMMA) (Neal *et al.*, 1992), which is applied to the Hafren stream to model temporal variability. ANC is used as a measure of stream chemistry, because it is conservative, and the model may be written as follows:

$$\frac{Q_{groundwater}}{Q_{streamwater}} = \frac{ANC_{streamwater} - ANC_{soilwater}}{ANC_{groundwate} - ANC_{soilwater}} \quad (1)$$

where Q represents discharge, ANC is the Acid Neutralisation Capacity and the subscripts *streamwater, soilwater* and *groundwater* each refer to those specified sources, the latter two being the identified end-members. The following assumptions are made in application:

   i. Streamwater consists of two 'end-members', each with a distinct chemical signature, which mix together.
   ii. The chemistry of the end-members changes very slowly over time (i.e. does not change during event responses).
   iii. The chemistry of the end-members may be estimated by sampling stream chemistry at extreme low and high flows.

To obtain estimates of Hafren end-member chemistry, weekly ANC data (n=829) are ranked according to flow, and the upper and lower 5% of values are selected. The average ANC of these two sets of values is calculated (-65 meq l^{-1} and 38 meq l^{-1} respectively), and used as soil and groundwater end-member chemistry in the model.

The stream hydrograph for 1996, represented by 15 minute discharge data, is split into the two flow components using a time series of ANC data. Although it is not possible to measure ANC *in situ*, measurements of pH are available at 15 minute intervals for 1996 (except for a period of 22 days during which instrument failure occurred). Data are converted to ANC using the equation of Robson (1993):

$$ANC = -102 + 113(\exp(-0.0042[H^+]) + \exp(-5.4[H^+])) \quad (2)$$

Figure 2 shows the calculated continuous ANC data plotted together with the spot sampled ANC which are calculated from Eqn. 3, where *Alk* is the Gran alkalinity (meq/l), *DOC* is in mg l^{-1} and Aluminium in mg l^{-1}. The continuous ANC fit these data well ($R^2 = 0.87$).

$$ANC = Alk + 54(DOC/12) - (Al/9) \quad (3)$$

By using the calculated 15 minute ANC data and end-member estimates, the groundwater flow proportion (GWP) for 1996 is calculated from Eqn. 1. Figure 2 shows the drop in proportion of groundwater flow during high flow periods when streamwater is typically acidic. The groundwater proportion does not always lie between 0.0 and 1.0, since some of the continuous ANC data lie outside of the estimated end-member range. These proportions are unrealistic but do not affect modelling predictions directly. Therefore, although corrections may be made by widening the end-member range (e.g. Hodgson and Evans, 1997) this is not undertaken here.

The rapid increase of groundwater proportion of flow during storm events suggests that this contribution is due to shallow groundwater rather than a deep, slow-responding
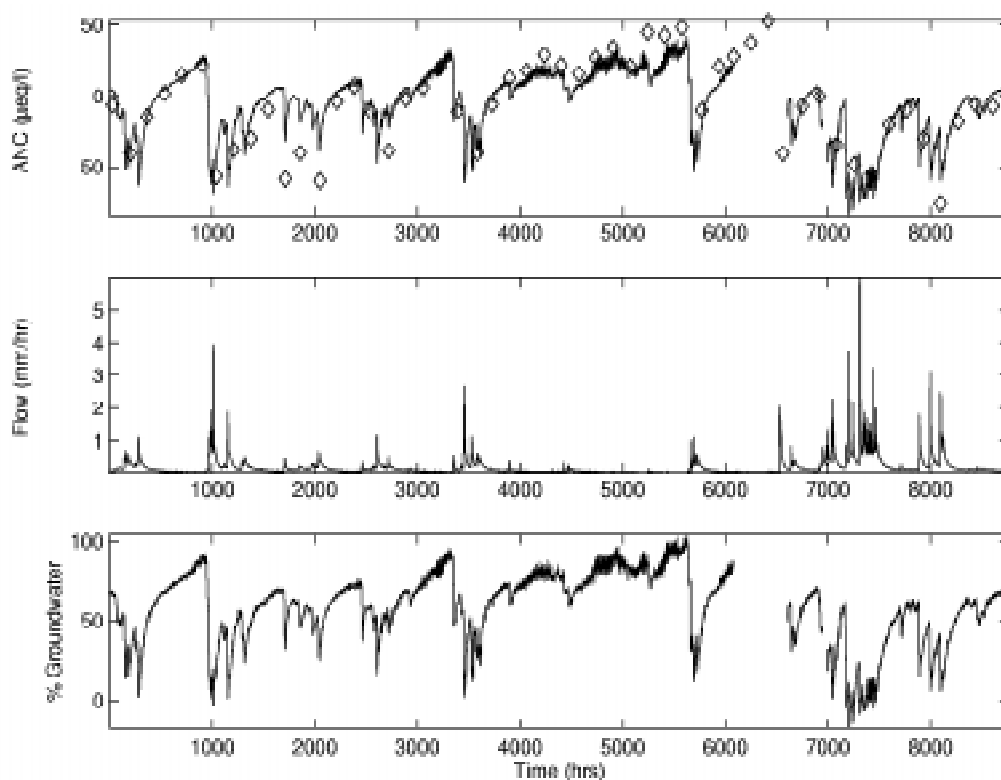
Fig. 2. *Continuous ANC data, flow and the calculated 1996 hydrograph split for the Hafren, specified by groundwater proportion of flow.*

component. This is consistent with the fact that the effect of forestry is seen even at low flow at Plynlimon (Foster *et al.*, 2001). Although fracture flow through the deeper bedrock could explain the rapidity of storm base-flow response and deep groundwater flow is known to exist in the Plynlimon catchments (Hill and Neal, 1997; Neal *et al.*, 1997), the observed deep groundwater chemistry has much higher alkalinity than the observed end-member. The ANC and groundwater proportion time series data are converted into duration curves by ranking the values and plotting in terms of percentage of time that a certain value is exceeded. These duration curves summarise the variability in stream ANC and groundwater proportion of flow and are used as a basis for representing temporal variability in the subsequent modelling stages.

Extension of EMMA to incorporate spatial variability in stream chemistry

Variability of soil type, bedrock mineralisation and land-use across the Plynlimon catchments results in different temporal responses being observed at each monitored site (Reynolds *et al.*, 1986, 1988; Foster *et al.*, 1997). This implies that although discharge is the dominant control on hydrochemical variation at a given site, the variability of catchment characteristics between sites has to be considered when modelling the whole area. This spatial dimension to the variability may be assessed by considering the variability of extreme flows, considered representative of the end-members, at a range of sites. Low flow spot samples are available for 40 sites, and weekly chemistry for 10 (Fig. 1); the latter may be used to calculate a soilwater end-member by averaging the top 5% of flow values, as for the Hafren. Plotting ANC against cumulative upstream drainage length reveals the extent of this variability, with ANC ranges of –93 to 217 meq l^{-1} for low flow and –114 to 5 meq l^{-1} for high flow (Fig. 3). Examination of Fig. 3 reveals great heterogeneity, especially for first order streams, although this tends to reduce with distance downstream. At these small scales, base-flow chemistry is found not to have a constant or predictable composition, for example from catchment characteristics such as soil and land-use type (Foster *et al.*,
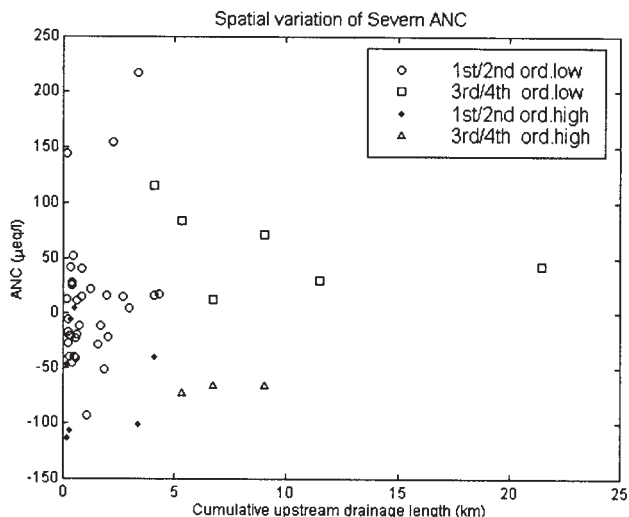
Fig. 3. *Spatial variability in low and high flow stream ANC in the Severn catchments.*

2001). Figure 3 also reveals that the high flow chemistry is spatially variable and that the standard deviation decreases as the stream order increases. This variability must therefore be incorporated into the EMMA and since deterministic prediction at site is precluded, a way forward is to quantify the end-members in terms of statistical distributions and input them to the EMMA model using Monte-Carlo analysis.

An application is made to the whole Severn catchment using distribution approximations of the groundwater proportion data and the end-member data sets. The low flow samples are extrapolated linearly between sites so that a value is calculated for each 25 m reach; hence, these values may be considered to represent the groundwater end-member variability along the stream length of the catchment. The data approximate to a normal distribution with a calculated mean and standard deviation of 12 and 50 meq l^{-1} respectively. There are too few high flow samples to allow extrapolation, so their mean (–61) and standard deviation (41) are calculated for use in an assumed normal distribution representation.

The time series data of groundwater proportion from 1996 are represented by using an exponential transformation of the data which approximates them to a normal distribution. The calculated mean and standard deviation of the transformed data are then used to define the distribution. Because values are selected from given distributions of parameters at random and then run through the model, the results represent the full range of likely scenarios given the variability of the input parameters. Fixed time intervals for groundwater proportion (GWP) are selected for computational efficiency and to ensure easy plotting of results.

Stream ANC values for each simulation are calculated from Eqn. 4:

$$ANC_{streamwater} = ANC_{groundwater}(GWP) + ANC_{soilwater}(1\text{-}GWP) \quad (4)$$

The method is applied as follows:

i. The groundwater proportion (GWP) duration curve calculated from the continuous data is approximated by a cumulative distribution and represents temporal variability. It is considered representative of all sites across the catchments.

ii. For given increments in proportion of time on the GWP duration curve (e.g. 1%) the relevant GWP value is selected.

iii. 2000 end-member pairs are randomly selected from the normal distributions approximating the spatial distribution of each, where $ANC_{soilwater} < ANC_{groundwater}$.

iv. Selected end-members are input to Eqn. 4 to produce 2000 ANC values which are considered to represent the spatial variability in ANC. These are ranked to show the percentage of stream length along which ANC is exceeded at a given time.

Application of this method results in a 'surface' of ANC consisting of a number of ANC duration curves for changing GWP (Fig. 4). Therefore, ANC values are a function of time and 'space' where space is actually represented by stream length. A contour plot of this surface is shown in Fig. 5 and may be used to assess the current stream water quality. For example, an ANC value of 0 meq l^{-1} is exceeded for 90% of the time along 10% of the catchment stream length. This
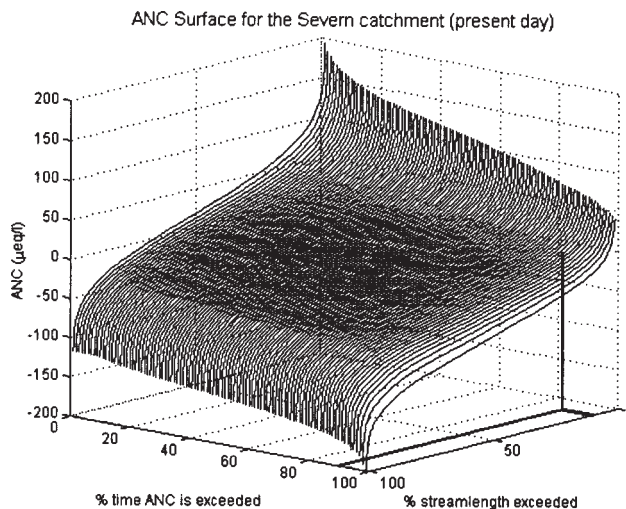

Fig. 4. *ANC surface plotted as a function of time and stream-length over which each value is exceeded.*
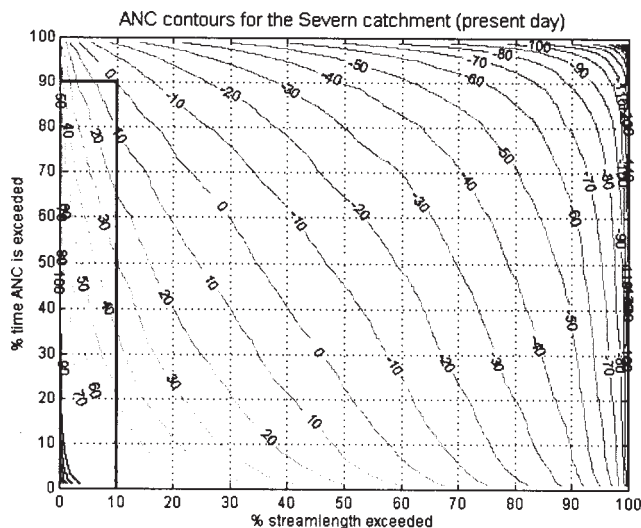
Fig. 5. *Contour plot of ANC values as a function of time and stream-length over which they are exceeded.*
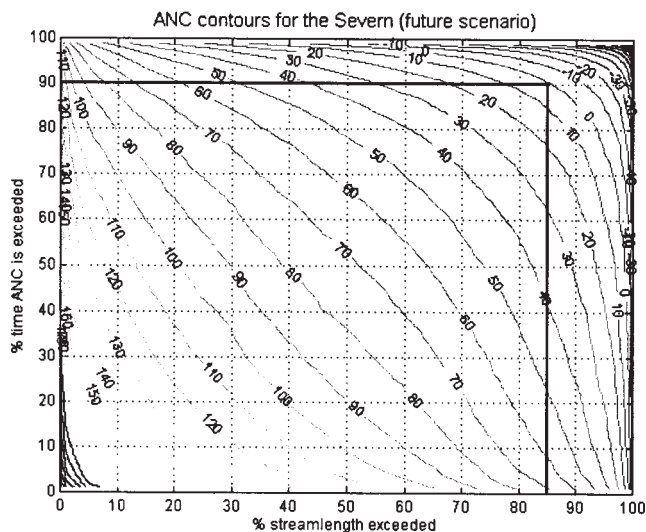

Fig. 6. *Future scenario contour plot using end-members 'evolved' in MAGIC for 2041.*

new methodology is thus more appropriate for assessing catchment hydrochemistry than methods which account for the average annual ANC representing the catchment as a whole, and do not incorporate either temporal or spatial variability.

Predicting future scenarios using MAGIC

Future scenarios of temporal variability may be predicted by considering the chemical changes in the end-members with time under given pollutant deposition and forest scenarios. MAGIC is used to calculate changes in an upper and lower soil layer, the chemistry of which is considered to represent the two end-members. Stream chemistry data are not available at the Severn catchment outlet and so the model is calibrated to Hafren stream data. Weathering rates, nutrient uptake and initial soil exchangeable fractions of base cations are adjusted to achieve a successful calibration, whereby stream major anion and cation chemistry is matched to within $3\,\text{meq}\,\text{l}^{-1}$ and soil and stream ANC to within $1\ \text{meq}\ \text{l}^{-1}$ (Foster, 2000). By way of illustration, a future scenario is run to predict soil and stream chemistry in the year 2041, using methods outlined by Jenkins *et al.* (1997a). It is assumed that the forest trees mature and are felled at 50 years of age without replanting, and that pollution deposition adheres to the Second Sulphur Protocol, whereby national S emissions are reduced by 70% of 1994 values by the year 2005 and 80% by 2010.

The modelled end-member ANC values change from –65 to –2 meq l^{-1} for the upper layer and 39 to 115 meq l^{-1} for the lower layer for the future date. The forest felling and decrease

in sulphate deposition hence result in a significant increase in ANC for both stream and soil.

EMMA is then undertaken for the future scenario using the new end-member chemistries. Two assumptions are made as a starting point for the application:

i. Hydrological conditions in the catchment do not alter over time
ii. The standard deviation of end-members remains constant during the period of change

Normal distributions are used to characterise the 'future' end-member compositions using the new mean values and previous standard deviations. The ground-water proportion duration curve for 1996 is used to produce new ANC duration curves by selecting values from the two end-member distributions as before. The resulting ANC surface is contoured and shown in Fig. 6. It can be seen that an ANC of 0 meq l^{-1} is now exceeded for 90% of the time along approximately 75% of the catchment's stream length. This is a major improvement of water quality as a result of the pollution abatement strategy.

Discussion

Both temporal and spatial stream-water chemistry variability within a catchment have been assessed jointly. Previously these have been treated almost entirely in isolation; studies that have considered both have tended to concentrate on a regional rather than catchment scale. However, when

considering the impact of pollution abatement strategies on surface water chemistry, particularly in the context of surface water acidification problems and protection of environmental systems, the small scale effects are important (Coric, 1999; Jenkins *et al.*, 1997b). Stream-water chemistry is unpredictable, being essentially random at the scale of the Plynlimon catchments (Neal and Reynolds, 1998), and the method presented here is able to incorporate such hydrochemical variability.

Two-component mixing End-Member Mixing Analysis (EMMA) has been shown to be a simple but powerful tool for predicting future stream-water chemistry when linked to MAGIC, as illustrated previously at Plynlimon by Neal *et al.* (1992). The extension of the EMMA method in this paper assesses stream ANC values as a function of time and stream-length. The modelling can predict the spatial variability of stream chemistry over both the long term (years) and short term (days). However, to retain simplicity, a number of assumptions have been made and the limitations of the method rest on the validity of these.

A basic assumption is that a two-component conceptual mixing model is an adequate representation of catchment response. The assumption of constant end-member chemistry along flow pathways and through time is challenged by some available field data. For example, Hoeg *et al.* (2000) assessed uncertainties in hydrograph separation using silica and ^{18}O at the Zastler catchment, Germany, which were considered to be due primarily to changes in end-member composition during events. At Plynlimon, sampled groundwater in both shallow and deep boreholes, as well as in emergent surface runoff at Plynlimon is chemically dynamic, which appears to invalidate a constant end-member component (Hill and Neal, 1997; Neal *et al.*, 1997a). Chemical changes along flow pathways have also been observed in a small moorland sub-catchment of the Wye (Chapman *et al.*, 1993, 1997; Muscutt *et al.*, 1993). However, observed stream chemistry is relatively consistent at high and low flows and does not reflect the temporal variability observed in deep groundwater or the spatial variability observed in soil chemistry at Plynlimon (Foster, 2000). Therefore this assumption holds to a first approximation for streamflow at the scales considered here. (An intensive storm event sampling programme would be required to assess further the errors in hydrograph separation).

The high flow end-member may, therefore, be considered to represent an integrated measure of soil water chemistry (Foster *et al.*, 1997) and the same may be considered for groundwater. If changes occur along flow pathways, then the end-member may be considered as representing the water chemistry as the end of the pathway rather than at the beginning. This is illustrated by a study at the Panola

Mountain Research Watershed, Georgia (Hooper *et al.*, 1998), where chemical changes of end-members took place *en route* to the stream. The riparian zone was found to be the dominant control on stream water chemistry and the geographical extent of the end-members was confined to this area. Sampling of hillslope waters during events showed them not to make a large contribution to streamflow. However, EMMA was still a useful modelling tool and stream chemistry reflected changes in the A-horizon end-member over a four year period, generally supporting the mixing hypothesis. For the purposes of the current application, EMMA is considered an adequate representation of the system, as correct representation of the stream chemistry is the aim, rather than an assessment of where the end-members originate.

A related issue is whether the two-component model may be too simple to represent fully the flow-pathways, as some other studies have required three end-members to model the system (e.g. Genereux *et al.*, 1993). However, the relative consistency of observed end-members, discussed above, and the associated analysis supports the validity of the two component approach as a reasonable first approximation. A more complex model would require additional tracer data and would be extremely difficult to incorporate within the modelling framework developed here, especially if non-conservative behaviour has to be considered. In application, the uncertainty in the calculated end-members and modelled stream ANC also needs to be considered. The estimation of end-members depends upon the 'cut off' point chosen (arbitrarily) for end-member representation of the stream chemistry data.

In addition to the limitations of the conceptual model, errors also exist within the data utilised, especially the ANC/pH relationship upon which the modelling relies. Although there is a strong correlation between ANC and pH, scatter is evident and, occasionally, the rainfall pH signal is observed in the stream during large events (Robson *et al.,* 1993) which may not be reflected in the observed ANC. Inevitably this leads to some errors. However, if the data are used to model a 'typical' response rather than the specifics of any event, then these data are adequate.

Despite its limitations, the method provides a way of considering the effects of catchment heterogeneity within a modelling framework by incorporating small-scale stream chemistry variability. Using Monte-Carlo techniques enables assessment of the likely variability throughout the catchments. Because the method is data-driven, the more data that are available, the more an accurate picture can be obtained. The model can also be updated easily as more data become available, for example by adjusting the distributions from which the end-members are selected.

Prediction of stream chemistry as a function of time and space has a number of advantages. It enables assessment of what proportion of streams in the catchment may have conditions which are hostile to certain biological organisms and provides a more detailed picture that may be used for biological research purposes. The ANC duration curve used in this methodology has been shown to be a good means of predicting the presence or absence of fish in streams (McNish and Harriman, 2000). Therefore, the method is potentially a powerful tool by which biological diversity both within and between catchments may be correlated with hydrochemical variability.

Robson (1993) used a chemical speciation model, ALCHEMI, to predict concentrations of non-conservative elements using EMMA, in addition to ANC. This could be used to extend the method to produce surfaces of other determinands of interest, such as aluminium, pH or Ca, dependent upon the data required for biological predictions. End-member standard deviation generally decreases as stream order increases (Fig. 3); therefore the method may also be applied to streams of different order, depending on the habitat of biota that are to be protected. In addition, the proportion of stream-length and time that a certain ANC value is transgressed under future deposition scenarios is predicted. This provides a potentially powerful tool for assessing the biological impact of future deposition scenarios which includes a measure of episodicity.

Because the method links EMMA to a process-based model that describes the relationship between acid deposition and end-member chemistry, the combined methodology may underpin future policy decisions. MAGIC has already been used extensively to calculate critical loads to predict the deposition reduction required to meet a mean stream chemistry ANC. For example, the method presented here may be used to produce, by iteration, the deposition reduction required to maintain the stream ANC above 0 for 80% of the time, as opposed to just calculating a mean annual value. This improvement begins to address some of the concerns about current policy decision making, which do not account for sub-catchment spatial variability.

The method has the flexibility to be applied to other catchments or regions. The Plynlimon catchments are typical of upland areas which are greatly heterogeneous in their physical properties. This means that, at the small scale, the system is highly unpredictable. However, as scale increases, an 'integration' of variability takes place. This occurs on both the micro- to macropore scale as discussed above, and on the sub-catchment to regional scale. As catchment size increases, it becomes a more valid approximation to consider the catchment to consist of one or more homogeneous units of a certain soil-type or land-use which will dominate the hydrochemical response. This is supported by the success of predictions of chemistry in large catchments using catchment characteristics as a basis (Wade et al. 1999; Cooper et al., 2000). Therefore, for a large catchment application, it may be necessary to apply the MAGIC model to different soil types and then to mix the resulting end-members together as illustrated by Wade (1999). This is not appropriate at the small catchment scale because of the insignificant relationship between soil type and stream chemistry (Foster et al., 2001).

Conclusion

A method for combining the prediction of the variability of catchment stream chemistry in time and space has been outlined. Temporal variability is modelled using EMMA, which is extended to incorporate spatial variability in end-member chemistry using Monte Carlo analysis. Spatial distributions of the two end-members are required; these are estimated from available field data and are input to EMMA as stochastic variables. ANC duration curves, each produced from a large number of input end-member pairs, are calculated for different points in time and used to produce an ANC surface. From this, a percentage time and stream length that a certain ANC value is exceeded may be estimated.

In this way, a picture is given of the catchment hydrochemical variability. This may be used to predict catchment biodiversity and how this may change over time given changes in distributions of the end-members, which are predicted by MAGIC. The conceptual model on which the modelling is based, consisting of two flow components of 'soil-water' and 'ground-water' flow, is a significant simplification of a complex system. However, the limitations of the method are counterbalanced by the major benefits of being able to assess variability in both time and space. Existing methods used as a basis for policy decisions cannot account for both the spatial and temporal variability, but rather address one or other. The development of this method is therefore considered to be an important step forward in the modelling of small heterogeneous catchments for management purposes.

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