ASSESSMENT OF THE SPATIAL HETEROGENEITY OF WEATHERING RATES IN UPLAND CATCHMENTS USING THE SODIUM DOMINANCE INDEX AND ITS SIGNIFICANCE IN INTEGRATED CATCHMENT MANAGEMENT

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ABSTRACT

The sodium dominance index was developed to quantify weathering rates and critical loads in Scotland, where atmospheric aerosols of maritime origin dominate over biogeochemical weathering in providing base cation inputs to catchment soils and drainage waters. Thus high sodium dominance in river or lake water indicates low weathering rate. We have further evaluated this concept using intensive temporal and spatial sampling strategies in two substantial catchments, the Dee in north east Scotland and the Etherow in central England, with particular reference to detection of groundwater inputs, and to possible problems from road salting in the calibration. In the Dee network, the spatial distribution of sodium dominance reflects the distribution of soil parent material geology, but land use also influences the equations. It is postulated that road density, via winter road salting, influences the sodium dominance calibration in lowland agricultural areas. Although road salting can also be problematic in some upland areas, the index still can provide clear indication of the likely severity of acid flush events in remote upland streams. In the Etherow catchment, sodium dominance varies markedly, sometimes over relatively small distances, reflecting soil type distribution, the occurrence of ground-water inputs to streams, and the influence of water in tributaries above the sampling point.

Key words Sodium dominance index; integrated catchment management; weathering rate; heterogeneity.

INTRODUCTION

It was suggested in 1999 that, in GB uplands, the extent to which the soluble base cations in rivers are dominated by sodium of oceanic aerosol origins provides an integrated measure of soil mineral weathering rates in a catchment above the sampling point (White *et al*., 1999). The idea originated from a study of waters draining peaty catchments in north and north-west Scotland. For streams in this area it was shown that the ratio of Na to ΣNa + Ca + Mg (concentrations expressed on a moles of charge basis) was virtually identical for both precipitation and consequential drainage waters, because both equilibrated with the peat (Cresser *et al*., 1997, Dawod and Cresser, 1997).

Recently we have calibrated the sodium dominance index quantitatively for north-eastern Scotland against annual weathering-derived alkalinity and base cation fluxes leaving catchments, using data from 59 Scottish rivers (Stutter *et al*., 2002). The calibration was appreciably better for annual alkalinity flux (R^2=0.831) than for the annual base cation flux (R^2=0.633, n=37), due to the role of non-marine sulphate and dissolved organic matter in base cation transport (Stutter *et al*., 2002). The capability of the Na dominance index to predict alkalinity fluxes prompted White *et al*. (2000) to investigate its applicability for prediction of critical loads of rivers in upland catchments under diverse flow regimes. Using data from 30 independent catchments in Scotland, they developed multiple-linear regression-based equations which predicted critical load values under base flow and high flow conditions, and for annual mean data from bi-weekly sampling, from natural logs of sodium dominance index values and of catchment maximum altitude. The equations were validated using data from a further 20 catchments, yielding R^2 values between predicted and observed values of 0.87, 0.74 and 0.89 for mean, base flow and high flow data, respectively (White *et al*., 2000).

The success of the calibration for predicting annual alkalinity flux suggests that the sodium dominance index could, once calibrated, provide a simple and inexpensive approach to quantifying the spatial distribution of weathering rates within a catchment. It therefore further suggests that it is potentially a powerful tool for use in integrated catchment management programmes for deciding upon optimal land use and soil management strategies for surface water protection.

Before applying the proposed calibration equations for weathering rate to other regions of the UK or Europe, it was deemed necessary to consider potential sources of error in applying the weathering index. In particular it was thought necessary to consider: (1) to what extent road salting in winter might limit the applicability of the technique; (2) why upland and agricultural (generally predominantly lowland) catchments yielded different calibration equations, and why the difference between equations for upland and agricultural catchments was far more pronounced for annual fluxes of base cations than for annual fluxes of alkalinity (Stutter *et al*., 2002); and (3) how readily ground water inputs could be detected. These issues will be explored by: (1) Studies of localized salting problems at selected sites on the North York Moors, where small salt piles are deposited beside the road for use as required in winter, often at bends, steep hills and bridges; (2) re-examination of data from the river Dee catchment in north-eastern Scotland; and (3) evaluation of data for the River Etherow catchment, between Barnsley and Manchester in northern England.

SITES AND METHODS

Data (unpublished) used in the evaluation of localised salting problems and for preliminary assessment of detection of groundwater input was colleted by Dorothy Dahl for Bonfield Gill and the River Riccal, in N. Yorkshire. Bonfield Gill passes over several different types of parent rock from the Middle Oolite geological series. It was anticipated, therefore, that there would be differences in the value of the index as the surface water percolates through material with different weathering rates. The river is influenced downstream by groundwater springs, which emanate at the base of calcareous rock above impervious strata. These were expected to add to the spatial variation in the Na dominance value compared to that of water draining directly off unimproved peat moorland. Some afforestation occurs beside the river in the mid altitudinal zone. Bonfield Gill disappears in a series of swallow holes in dry weather, and re-emerges further down the dry water course as the River Riccal.

As road salting was considered to be a possible complicating influence, rivers were sampled above and below road bridges, to detect what difference salting made. The site locations are listed in **Table 1**. Bonfield Gill has its source above Botany Bay, and sinks just below the Pockley site. Downstream of this sink, the mapped river bed was dry at time of sampling, though there was evidence that, under higher flow conditions, it carries water. The River Riccal has its source at Riccal Bridge. Where roads crossed the rivers, river water samples were taken at places *ca.* 20 m upstream and downstream of the bridges, to detect any influence of road salting.

The data for the Dee catchment in Scotland were obtained by sampling at 59 points, mainly at lower reaches of headwater streams, but with 6 points on the main river system, bi-weekly over one year. Characteristics of the catchments and analytical methodology have been discussed elsewhere (Langan *et al*., 1997, Smart *et al*., 1998). Weathering rates were calculated by the catchment input/output balance approach (Reid *et al*., 1981, Hornung *et al*., 1985, Hyman *et al*., 1998).

The River Etherow catchment lies in the altitude range 300 m to 633 m OS. The catchment comprises *Calluna* and *Vaccinium* moorland with patches of grassland (*Agrostis* and *Molinia*) and some areas of deciduous woodland. *Juncus* is abundant on wetter areas. The lower slopes contain improved and rough grazing, mainly used for sheep. The upper areas are mainly grouse moor. The underlying parent material is millstone grit interspersed with bands of marine deposited mudstone. Mean annual rainfall is 1480 mm.

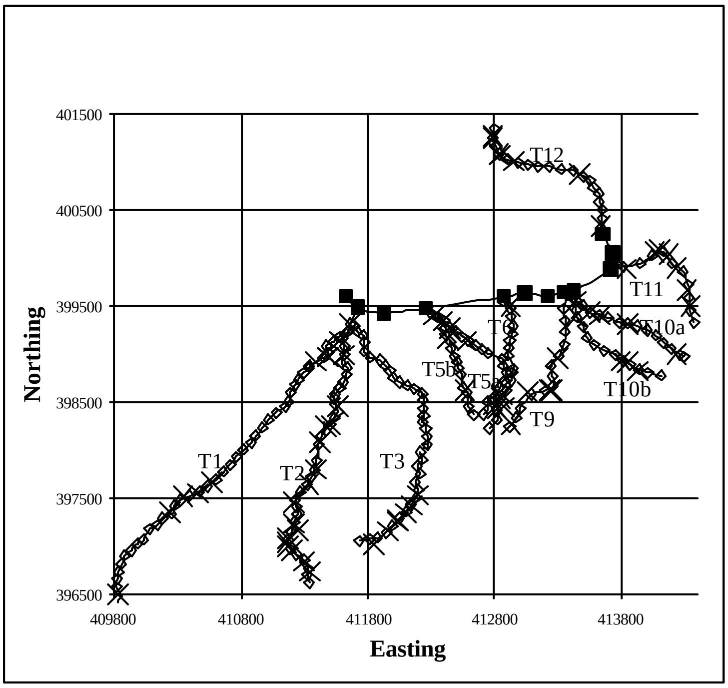

Figure 1 *Sampling points used in the Etherow catchment. (■) , main stem monthly sampling points, (◇), main tributary sampling points, and (✕) extra tributaries sampling points.*

Stream-water was sampled monthly over 18 months along the main stem of the Etherow, and its main tributaries just upstream confluence points, as shown in **Fig. 1**. During late May and early June of 2001, a high intensity sampling was also carried out at the Etherow catchment. Over 300 samples were taken at 100-m intervals along all the main tributaries (Fig. 1). The weather over this period was very dry, in accordance with the forecast at the time. This was deemed to be important, as the alkalinity flux predictions made for Scotland used data for the three lowest base-flows, which correspond to prolonged dry periods. All samples were analysed for pH, alkalinity, NH_4-N, NO_3-N, organic-N and the major cations and anions.

Table 1 The location of the water sampling sites on Bonfield Gill and the River Riccal. The grid references, elevations above sea level, geology, soil types and vegetation in the immediate vicinity of the sites are provided. Sites 1 to 4 are on Bonfield Gill, while 5 and 6 are on the River Riccal.

Site No.	Site Name	O.S. Grid Ref.	Ht. (m) above sea level	Geology	Soil Type	Vegetation
1	Botany Bay	SE 603955	300	Sandstone	Cambic stagno-humic gley	Heather moor, with grass next to river
2	Bonfield Gill	SE 608942	240	Sandstone and shale	Cambic stagno-humic gley	Heather moor, with a few trees along river
3	Cinderhill	SE 612913	215	Sandstone, shale, and Ellerbeck Bed ironstone	Podzol with iron-pan	Heather moor and enclosed improved grassland
4	Pockley	SE 628859	70	Limestone	Brown earth	Forestry on steep valley sides
5	Riccal Bridge	SE 633842	55	Alluvium overlying Kimmeridge Clay	Brown earth	Forestry with some arable
6	Lower Riccal	SE 673806	30	Alluvium	Brown earth	Arable, with trees along river

RESULTS

Figures 2 and 3 show how pH and Na dominance varied on progressing downstream from Botany Bay on Bonfield Gill to the lower River Riccal, on 14/02/2000 and 28/02/2000, respectively.

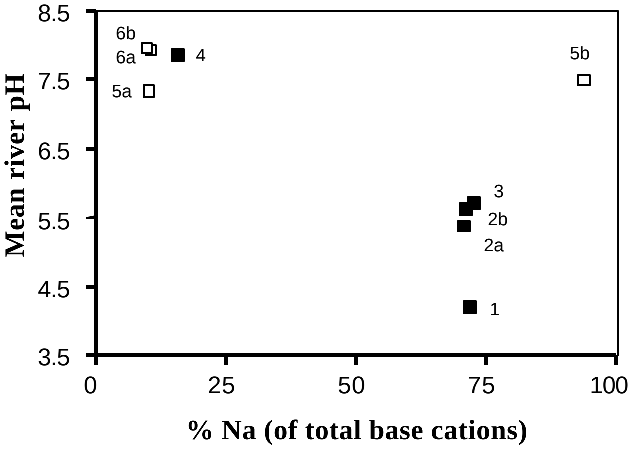

Figure 2 *Relationships between mean river water pH and the relative contributions of* Na^+ *to S*$Na^+ + Ca^{2+} + Mg^{2+}$ *for the catchments of Bonfield Gill (n) and the River Riccal (•) for samples taken on 14.02.2000. Nos. 1-6 refer to sites listed in Table 1, and a and b to sampling points upstream and down stream of a bridge crossing the river, respectively. Salt piles were seen either side of Riccal Bridge (site 5).*

If data for the sites immediately downstream from bridges are excluded, the R^2 values for the regression equation between pH and Na dominance were 0.873 and 0.875 on the two sampling dates respectively.

Figure 4 shows the difference between regression equations linking log Na dominance at baseflow in sub-catchments of the River Dee drainage basin in Scotland to annual fluxes of alkalinity in the river systems sampled. It is very noticeable that the agricultural catchments generally give higher Na dominance that would be expected from the observed alkalinity flux.

Spatial distributions of Na dominance and pH values for two of the tributaries (T1 and T5a in Fig. 1) monitored in the intensive sampling programme at the Etherow catchment, and Na dominance values for additional minor tributaries confluent with T1 and T5a, are shown in Fig. 5. For T1, which drains very mixed soil types, Na dominance is highly variable, much more so than water pH. For T5a, which predominantly drains peat throughout most of its length, Na dominance is consistently high, and pH consistently low, except low down in the catchment where Na dominance falls slightly and pH starts to rise.

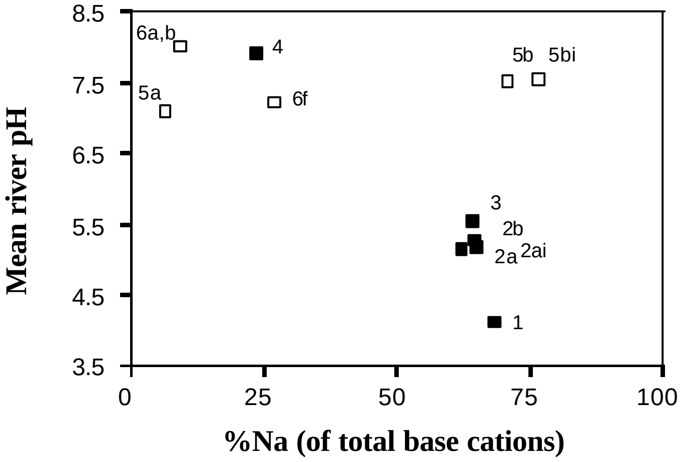

Figure 3 *Relationship between mean river water pH and Na dominance on 28.02.00 (n=3). The sites sampled in addition to those sampled on 14.02.00 were 2ai, a short distance upstream from site 2, 5bi, a little further down the R. Riccal from 5b at Riccal Bridge, and 6f, a field drain, between Site 6a and the road bridge at Lower Riccal. Symbols are as in Fig. 2.*

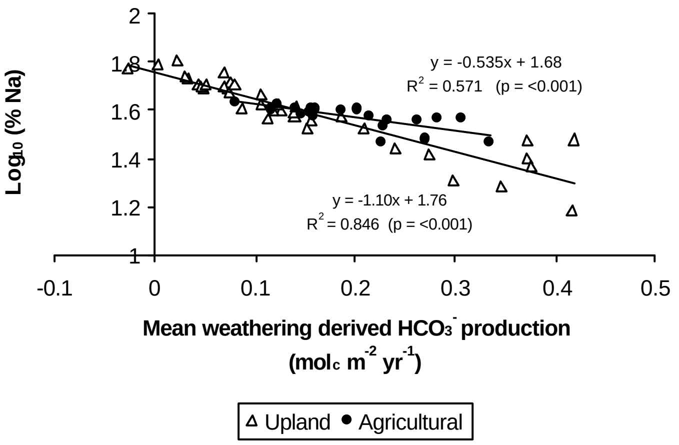

Figure 4 *Relationships between log Na dominance and annual flux of alkalinity for independent upland (no agricultural improvement) and agricultural sub-catchments of the River Dee drainage basin, based upon data reported by Stutter, Smart and Cresser (2002).*

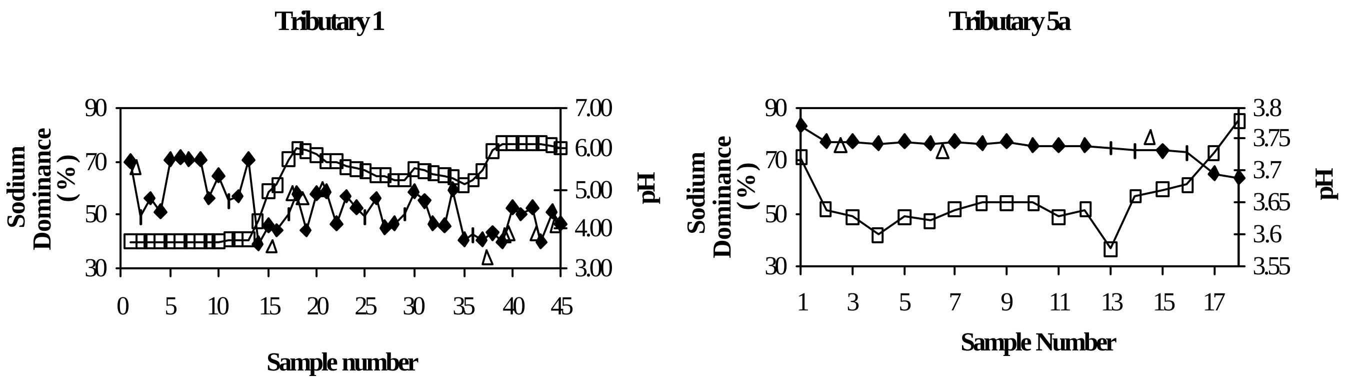

Figure 5 *Spatial distributions of pH (☐) and Na dominance (¨) along the length of two of the major tributaries to the River Etherow shown in Fig. 1. Also shown are Na dominance values for minor tributaries flowing in to T1 and T5a ( )).*

To test how long road salt effect might last, time series plots were drawn comparing molar Na^+ and Cl^- concentrations for sampling points in Dee and Etherow catchments known to be at high risk and low risk of road salt contamination. The results are shown in Fig. 6.

DISCUSSION

Provided the data for sites obviously being impacted by road salts are ignored, the results presented in Figs. 2 and 3 show a very consistent relationship between acidity and sodium dominance, which is also similar to that presented in earlier work (White *et al*., 1998). The points in the North York moors study lie on the same graph as was obtained for northeastern Scotland under high discharge conditions, and the sampling in Bonfield Gill and the River Riccal was also conducted under very wet conditions. On both sampling dates, the impact of the localised road salt contamination is immediately obvious in Figs. 2 and 3. However, this was due at least in part to small piles of road salt dumped at Ricall bridge for use as and when required. The question remains, however, about whether lower but significant levels of contamination arise a consequence of salt spreading along roads, which often run parallel to rivers for long distances. Smart *et al*. (2000) have developed a model for prediction of spatial distribution of chloride concentration in Deeside rivers. They found that chloride concentration could not be explained simply in terms of atmospheric deposition of maritime-derived salts, and was significantly correlated with agricultural land use cover in individual sub-catchments studied. However chloride from fertilizer use could not nearly account for the extra chloride apparently associated with agriculture. They postulated that the extra chloride was a result of road salting, and the apparent link with agriculture for Deeside was an artefact of the greater road density in the lowland, agricultural areas. This postulate could well explain the results shown in Fig. 4, where Na dominance is higher than would be expected in agricultural, lowland areas.

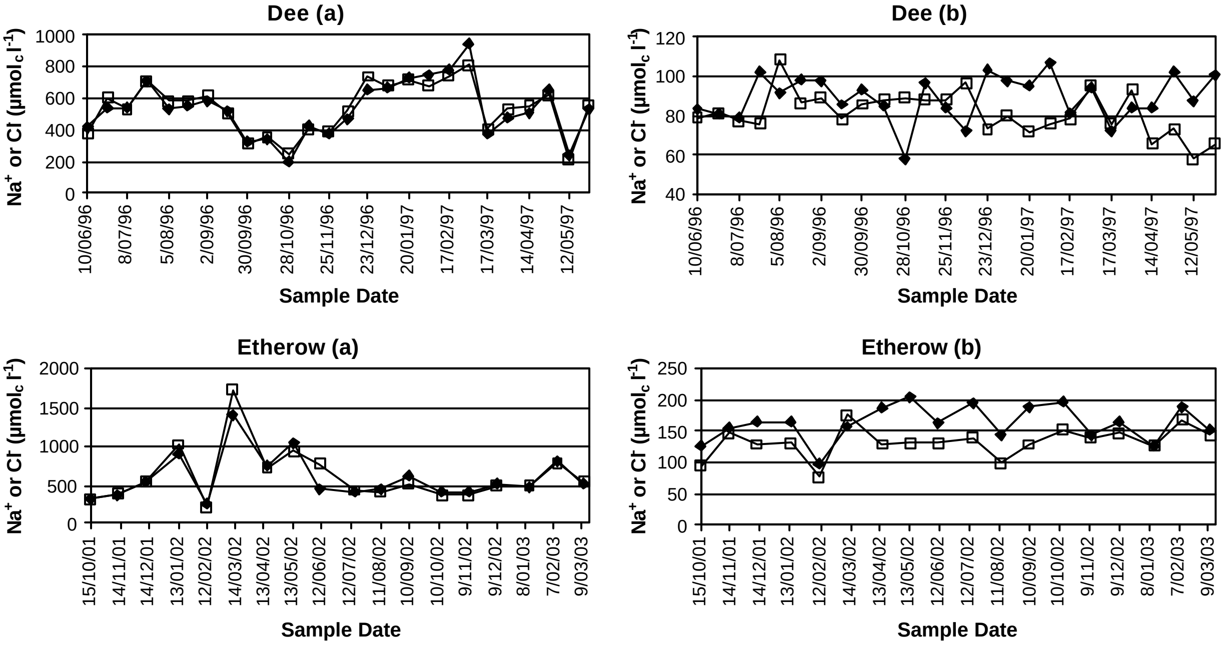

Figure 6 Effects of Road Salting

Unlike the sampling of Bonfield Gill and the Riccal, the Etherow intensive sampling was completed under low baseflow conditions. The results in Fig. 5 fit well with the extrapolated base flow pH *vs.* Na dominance plots for Scotland in earlier work (White *et al*., 1998). Tributary 5a drains peat almost throughout its entire length, so has a low pH (3.55 - <3.8) and a very high to high Na dominance, except at the lowest sampling points, 17 and 18, where the mineral soil starts to have a slight influence. The soils surrounding tributary 1 are much more variable, ranging from peats and peaty podzols to cambisols on mid to lower slopes. As a consequence, the Na dominance is much more spatially variable in this tributary, and visual observation of the raw data clearly showed that the change is driven almost entirely by spatial variation in calcium concentration, the concentrations of sodium and magnesium being much more constant spatially. The high Na dominance values, for example at the top of the catchment (sampling points 1, 5-8 and 13) were associated with water draining peat. Although the variation in Na dominance appeared to be closely related to visually observable soil type distribution, water inputs from tributaries, and their origins are also important. Data for some of these is included in Fig. 5.

Bearing in mind the different concentration scales used in Fig. 6, it is clear that the effects of road salting on river water quality at contaminated sites persist throughout the year, and are not just apparent in the winter months. It is also obvious that at contaminated sites, the road salt totally dominates the Na^+ and Cl^- concentrations found, so the molar ratio stays close to unity. At uncontaminated sites the ratio of Na^+ to Cl^- is more variable throughout the year, reflecting variation in dominant sources of supply and sinks of the two ions.

In a previous study, White *et al.* (1999) were able to show that the Na dominance index could be applied consistently throughout northern Scotland. The results presented in this paper suggest that it may be equally effectively applied, under both high and low flow conditions, as far south as Yorkshire, provided care is taken to avoid stretches of rivers that are significantly impacted by road salting effects. If our interpretation of the reason for the divergent equations linking Na dominance and annual alkalinity flux is correct, *i.e.* if the divergence is due to higher road density in lowland areas, then the application of the index in catchment management should be confined to upland areas in which road impacts are minimal. In such areas, the index value may be used to assess risk of acid episodes in rivers. It may also be used to identify catchment areas where weathering rates are low, and where, as a consequence, afforestation, especially with conifers, is likely to result in substantial acidification of stream waters, or liming is likely to be beneficial to water quality.

CONCLUSIONS

Application of the sodium dominance index for assessment of integrated upstream weathering rates in catchment soils, for informing management decisions appertaining to acidification risk due to forestation, or for identification of zones of catchments that should be limed to protect water quality is shown to be possible over a very wide regional (national) scale. However, it is also shown that road-salting effects may be substantial and long lasting, and the risk of error may not always be immediately obvious just from casual visual observation of sites. Care is therefore needed when applying the index in catchment management.

ACKNOWLEDGEMENTS

We are indebted to the UK NERC and DEFRA (formerly DETR) for financial support for this research.

REFERENCES

Cresser, M.S., Dawod, A. and Rees, R.M. (1997). The relationship between Na:Ca:Mg ratios in precipitation and in river water draining from peats and associated soils. *Wat. Res.*, **31**, 2253-2260.

Dawod, A.M. and Cresser, M.S. (1997). The direct relationship between base cation ratios in precipitation and river water draining from peats. ? *Humic Substances, Peats and Sludges, Health and Environmental Aspects*, Hayes, M.H.B. and Wilson, W.S., eds., Royal Society of Chemistry, Cambridge, 288-298.

Hornung, M., Reynolds, B., Stevens, P.A. and Hughes, S. (1985). The use of stream solute budgets for estimating weathering rates and period of soil development in a small mid Wales catchment, In: P.A. Stevens (Ed.) *Welsh Soils Discussion Group Report No. 24*.

Hyman, M.E., Johnson, C.E., Bailey, S.W., April, R.H. and Hornbeck, J.W. (1998). Chemical weathering and cation loss in a base-poor watershed. *Geol. Soc. Am. Bull.*, **110**, 85–95.

Langan, S.J., Wade, A.J., Smart, R., Edwards, A.C., Soulsby, C., Billett, M.F., Jarvie, H.P., Cresser, M.S., Owen, R. and Ferrier, R.C. (1997). The prediction and management of water quality in a relatively unpolluted major Scottish catchment: Current issues and experimental approaches, *Sci. Total Environ.*, **194/195**, 419-435.

Reid, J.M., MacLeod, D.A. and Cresser, M.S. (1981). Assessment of weathering rates in an upland catchment, *Earth Surf. Process. Landforms*, **6**, 447-457.

Smart, R.P., Soulsby, C., Neal, C., Wade, A., Cresser, M.S., Billett, M.F., Langan, S.J., Edwards, A.C., Jarvie, H.P. and Owen, R. (1998). The factors regulating the spatial and temporal distribution of solutes concentrations in a major river system in N.E. Scotland, *Sci. Total Environ.*, **221**, 93-110.

Smart, R., White, C.C., Townend, J. and Cresser, M.S. (2000). A model for predicting chloride concentrations in river water in a relatively unpolluted catchment in the north-east of Scotland, *Sci. Total Environ.*, **265**, 131-141.

Stutter, M., Smart, R.P. and Cresser, M.S. (2002). Calibration of the sodium base cation dominance index of weathering for the River Dee catchment in north-east Scotland. *Appl. Geochem.*, **17**, 11-19.

White, C.C., Smart, R. and Cresser, M.S. (1998). Effects of atmospheric sea-salt deposition on soils and freshwaters in northeast Scotland, *Water Air Soil Pollut.*, **105**, 83-94.

White, C.C., Smart, R.P., Stutter, M., Cresser, M.S., Billett, M.F., Elias, E.A., Soulsby, C., Langan, S., Edwards, A.C., Ferrier, R., Neal, C. Jarvie, H. and Owen, R. (1999). A novel index of susceptibility of rivers and their catchments to acidification in regions subject to a maritime influence. *Appl. Geochem.*, **14**, 1093-1099.

White, C.C., Smart, R. and Cresser, M.S. (2000). Spatial and temporal variations in critical loads for rivers in N.E. Scotland: A validation of approaches, *Wat. Res.*, **34**, 1912-1918.